Statistical Mechanics

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Preface

A number of years ago I became aware of the large number of physics enthusiasts out there who have no venue to learn modern physics and cosmology. Fat advanced textbooks are not suitable to people who have no teacher to ask questions of, and the popular literature does not go deeply enough to satisfy these curious people. So I started a series of courses on modern physics at Stanford University where I am a professor of physics. The courses are specifically aimed at people who know, or once knew, a bit of algebra and calculus, but are more or less beginners.

This volume is based on notes prepared for a Continuing Education course I gave at Stanford in the spring of 2009, and for a graduate course in statistical mechanics that I gave at that same time.

– Leonard Susskind

I am one of those "physics enthusiasts," an engineer who grew tired of mass-market physics books shorn of all equations. I picked up the standard "Gravitation" text to try to teach myself general relativity, but even though I have a fairly good math background, it was too much. So I was delighted to find Prof. Susskind's course sequence at Stanford and to have the opportunity to help with the preparation of this volume.

– Warren Gibson

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1.1 Introduction

Statistical mechanics is often thought of as an approach to thermodynamics, or somewhat more generally, a theory of how atoms combine to form gases, liquids, solids, and even plasmas and black body radiation. But it is both more and less than that. It is more because it can be used in many areas of science where a large number of variables is involved – too many to address individually. In these cases statistical methods can be used to study the aggregate behavior of a system without knowing (or indeed caring about) the behavior of each element of the system. My son, who studies neural networks, uses it. "Financial engineers," often refugee physicists who sought fame and fortune on Wall St., perhaps with dubious results, also use statistical mechanics.*

So to say that Statistical Mechanics is the theory of gasses is rather like saying calculus is the theory of planetary orbits. That's how calculus may have started, but it has of course found vastly more applications. Although our examples will focus on thermodynamics and magnetics, other applications are possible.

1.2 Probability Theory

There are many good texts that explain the theory of probability, but for our purposes a few simple concepts will suffice. We will review them now starting with coin flipping.

The probabilities of a coin coming up heads (H) and tails (T) are both equal to 1/2. Why do we say that? Taking an *a priori* view, we can say that the physical symmetry of a coin allows us no reason to believe that either outcome is more likely than the other, so we must assign 1/2 to each probability. Taking an *a posteriori* view, we might flip a coin several thousand times and observe that we got heads (or tails) very nearly half the time and conclude that this will always be the most likely outcome.

Here is another example. Let's take a die (as in dice) and color the six faces red, yellow, blue, green, orange, and purple (R, Y, B, G, O, P). The cubic symmetry of the die dictates that the probabilities of any one face appearing on top when the die is rolled

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*J. Volt, "The Statistical Mechanics of Financial Markets," Springer, 2005

are all 1/6. Again, this is obvious from physical symmetry, or could be inferred from experiments. But what if we don't have an obvious symmetry to rely on? How do we assign *a priori* probabilities?

Suppose for example instead of the coloring scheme that I indicated above, I chose to color the purple face red. Then there would be only five colors. Would the probability of throwing a given color be 1/5? After all, if I just write (R, Y, B, G, O), the 5 names are just as symmetric as the original 6 names. Nonsense, you say: the real symmetry is among the 6 faces, and that is so. But what if there really is no obvious symmetry at all, for example if the die is weighted in some unfair way?

If we still wanted to pursue a theoretical or *a priori* approach we would have to rely on a bunch of details such as the precise way the die was thrown by the hand that threw it, the wind, maybe even the surface that the die lands of (can it bounce?). As is often the case, we have to think of the system in question as part of a bigger system. But what about the bigger system? How do we assign its probabilities?

Here is another idea that involves some dynamics. Suppose there is a rule that uniquely specifies the configuration of a system based solely upon its current configuration. We may call this rule a "law of motion," with time in this example proceeding in discrete steps. For example $R \to B$, $B \to G$, $G \to P$, $P \to O$, $O \to Y$, $Y \to R$ is such a rule (Figure 1). What fraction of the time does that die spend in each configuration?
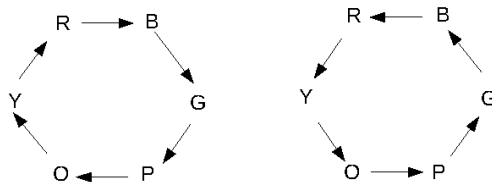
Figure 1: Two simple "laws of motion."

The answer is 1/6. In fact there are many possible laws for which the answer will be the same, such as $R \to B$, $B \to G$, $G \to P$, $P \to O$, $O \to Y$, $Y \to R$. or $R \to Y$, $Y \to P$, $P \to G$, $G \to O$, $O \to B$, $B \to R$.

But what about the rule $R \to B$, $B \to G$, $G \to R$, $P \to O$, $O \to Y$, $Y \to P$

(Figure 2)? In this case there are two trajectories through the space of states. If we

Figure 2: A law of motion with two trajectories.

are on one of them we don't ever jump to the other. So the probability will depend on where we started. We may wish to assign probabilities for beginning on either of the two cycles.

In this last case there is a conserved quantity. Suppose we assign the number one to R, B, G and zero to O, Y, P. Let's call this quantity the "Zilch number." Obviously Zilch is conserved. Whenever we have a conserved quantity like Zilch, we have to specify its value. That's not a problem, as there are many conserved quantities in nature, the most important in statistical mechanics being energy. Once we specify all the conserved Zilch numbers, we can proceed as usual, and say that all the states on a trajectory with a particular Zilch numbers are equally probable.

That sounds good, but there are lots of counterexamples. Here is one: $R \to R$ $B \to R$, $G \to R$, $P \to R$, $O \to R$, $Y \to R$. No matter where you begin, you go to red in the next instant and then stay there. There are no conserved quantities but obviously after the first step the probabilities are completely unequal; only red is possible.

This last law has something odd about it. It is an example of a law that does not respect the "conservation of distinction," or "conservation of information." In the previous examples distinct starting points always led to distinct outcomes. But in this case we quickly lose track of where we started. Trajectories merge!

One of the central principles of classical mechanics (and it has an analog in quantum mechanics) is that information (distinctions) is conserved. This principle is so important to the validity of statistical mechanics and thermodynamics that I would call it the "minus first" law of thermodynamics (the "zeroth law" is already taken.)

Later we will use an abstract concept called "phase space" in which the coordinates

represent not physical space, but variables that may be unrelated to space. For now, let's just note that conservation of distinctions says that trajectories in phase space never run into each other. Even stronger, if you start with a volume in phase space and follow it using the Hamilton's equations of motion, the volume is conserved. That suggests that for a closed system, *a priori* probability is uniform over the phase space. We will come back to this.

1.3 Energy

The First Law of Thermodynamics says is that energy is conserved. For a closed system,[†]

$$\frac{dE}{dt} = 0$$

If a system is composed of two very weakly interacting subsystems,[‡] the energy is additive:

$$E = E_1 + E_2$$

Interactions between the subsystems can exchange energy between them. Thus the energy of either subsystem is not conserved. In equilibrium the energy of a subsystem fluctuates although the total energy is fixed.

1.4 Entropy

Entropy is an information-theoretic concept. It is a measure of how much we *don't* know about a system. Our ignorance may stem from the fact that the degrees of freedom are too small to measure, too numerous, or too rapidly changing. The reason could just be our own laziness. In any case, entropy measures our ignorance.

Suppose a system can be in any of N states. If we know nothing about the state of the system (complete ignorance) the entropy S is defined as

$$S = \log N.$$

[†]A closed system is one with a time-independent Hamiltonian and with insulating walls so that no energy can enter or leave the system.

[‡]Weakly interacting means that the energy of interaction is very small compared to the separate energies of the subsystems by themselves. If the Hamiltonian is $H_1 + H_2 + H_{\text{int}}$, then the numerical value of H_{int} should be negligible compared with either H_1 or H_2.

Suppose we know only that the system is an any of M states with $M < N$. Then we have some nontrivial knowledge. In this case the entropy is defined to be

$$S = \log M.$$

Evidently, the more we know, the smaller the entropy.

Here are some further examples. Consider a system of n distinguishable coins. Each coin is in one of two states: H (heads) or T (tails). A state consists of an ordered sequence of H's and T's such as

$$H \; H \; T \; H \; T \; T \; H \cdots$$

Suppose we know nothing at all. The total number of possible states is 2^n and the entropy is

$$S = \log 2^n = n \log 2.$$

Note that by taking the log we have made entropy an extensive property, that is, proportional to the number of degrees of freedom n.

Entropy is measured in bits. If the entropy is $S = \log 2^n = n \log 2$, one says that there are n bits of entropy.

As another example, suppose we know everything that there is to know about the coins. In that case we know the exact state and $M = 1$. The entropy is $\log 1$ which is zero.

Next, suppose we know that $n - 1$ coins are in the state H and one is T, but we don't know which one. The system can be in any of n states and the entropy is

$$S = \log n$$

In this case the entropy is not additive but that is because there are strong correlations (to be defined later).

.... Homework ....

Problem 1.1 Suppose that n is even and that we know that half the coins are H and half are T, but that is all we know. What is the entropy?

Problem 1.2 For large n what is the entropy if we know that a fraction f of the coins are H and fraction $1 - f$ are T?

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In each case we are given a probability distribution on the space of states. If we label the states with index i then the probability that the system is in state i is called $P(i)$. In the examples $P(i)$ is zero for those states that are not possible and $P(i) = 1/M$ for the possible states. We can write a formula for S in terms of $P(i)$,

$$S = -\sum_i P(i) \log P(i). \qquad (1.1)$$

Those states with $P = 0$ contribute nothing and those with $P = 1/M$ contribute $(1/M) \log M$. Since there are M such states the sum gives $\log M$.

For a general probability distribution we require only that $P(i) \geq 0$ and

$$\sum_i P(i) = 1. \qquad (1.2)$$

The general definition of entropy is given by (1.1). Obviously each $P(i)$ satisfies $0 \leq P(i) \leq 1$ which implies that S is positive and that each contribution to (1.2) is positive or zero.

The entropy defined by (1.1) roughly measures the log of the number of states that have non-negligible probability in the distribution $P(i)$. In other words e^S is the "width" of the distribution. Note that the width is zero if and only if $P = 1$ for a single state and zero for all others.

.... Homework ....

Problem 1.3 Suppose you have a set of N coins. Each coin independently has a probability $1/3$ to be heads and $2/3$ to be tails. What is the total entropy?

Problem 1.4 A variable q has a uniformly spaced spectrum of values with very small spacing δ. The sum over states can be accurately approximated by

$$\sum_i \rightarrow \frac{1}{\delta} \int dq$$

Suppose the probability distribution for q is proportional to e^{-q^2}. What is the entropy?

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1.5   Temperature

The average energy associated with a probability distribution (call it E) is given by

$$E = \sum_i E_i P(i) \tag{1.3}$$

where E_i is the energy of state i.

Now suppose we have a one-parameter family of probability distributions labeled by the average energy $P(i; E)$. For each value of E, $P(i; E)$ satisfies the usual requirements of a probability distribution. Later we will think of it as the thermal equilibrium distribution for given average E. But for now it is just a one-parameter family.

At each value of E we can compute the entropy so that S becomes a function of E, $S = S(E)$.

Consider the amount of energy that is needed to increase the entropy by one bit (by $\log 2$). It is given by

$$\delta E = \frac{dE}{dS} \log 2 \tag{1.4}$$

We call the quantity dE/dS the temperature, T.

$$T \equiv \frac{dE}{dS} \tag{1.5}$$

We should think of temperature as follows:[§]

> *Apart from a factor of* $\log 2$, *the temperature of a system is the amount of energy needed to increase its entropy by one bit.*

For example, if you erase a bit of information from your computer you are really transferring it from the computer out into the atmosphere, where it shows up as some heat. How much heat? The answer is $T = \log 2$.

Except in very unusual circumstances, the temperature is always positive, i,e,. entropy is a monotonically increasing function of energy.

[§]Our definitions of temperature and entropy differ in essentially unimportant but potentially confusing ways from engineering definitions of such quantities. See Appendix D.

1.6   The Zeroth and Second Laws of Thermodynamics

The Second Law of Thermodynamics says that entropy always increases. We can state it more formally as

> When a closed system which is out of thermal equilibrium comes to equilibrium the entropy of the system increases.

We will come back to the reasons for this, but for now let's just accept it.

From the Second Law we can prove that heat always flows from hot to cold. Consider two isolated systems , A and B, at different temperatures. Their energies, temperatures, and entropies are $E_A, E_B, T_A, T_B, S_A, S_B$. Without loss of generality we can assume that $T_B > T_A$.

Now bring them into contact so that energy (heat) flows between them. Suppose a small quantity of energy is exchanged. The total change in energy must be zero. Therefore

$$T_A dS_A + T_B dS_B = 0 \tag{1.6}$$

Since they must tend to equilibrium, if the entropy is not maximum it must increase. Hence

$$dS_A + dS_B > 0 \tag{1.7}$$

We can use (1.7) to eliminate S_B from (1.6). We find

$$(T_B - T_A)dS_A > 0 \tag{1.8}$$

Since the system B is initially the hotter of the two, $(T_B - T_A)$ is positive. Therefore dS_A and also $T_A dS_A$ are positive. Equation (1.6) then tells us that $T_B dS_B$ is negative. Equivalently, energy flows from hot to cold as equilibrium is established. The final equilibrium configuration in which energy has stopped flowing must have $T_A = T_B$. In other words, temperature must be uniform in a system in thermal equilibrium.

2   The Boltzmann Distribution

If a system A is in contact with (weakly interacting with) a much larger system called a *bath*, then it can exchange energy with the bath. After a long time the combined system will have jumped around over all states having the given total energy. Each of these ways in which the energy can be shared will be equally probable. This is the assumption of *chaos* and although it is very difficult to prove for a given system, it is almost certainly true for almost all systems. Whenever it is true, the small system A will be in thermal equilibrium with a certain probability distribution for being in the state i. (Note that i refers to states of the small system A and not the combined system.)

We will illustrate the consequences of this principle by choosing the bath to be $N-1$ copies of A so that altogether we have a total system consisting of N copies of A. The copies are labeled $1, 2, 3, \cdots, N$ and they are in states $i_1, i_2, i_3, \cdots i_N$ with energies $E_{i_1}, E_{i_2}, E_{i_3}, \cdots E_{i_N}$.

Let us define the "occupation numbers" n_i to be the number of copies of A that occupy the state i. The n_i satisfy two conditions,

$$\sum_i n_i = N \tag{2.1}$$

and

$$\sum_i n_i E_i = E_{\text{total}}. \tag{2.2}$$

These equations state that the total number of copies adds up to N and that the total energy adds up to some fixed value, E_{total}. Keep in mind that i sums over states, not subsystems.

The assumption of chaos tells us that all of the configurations of the total system with a given total energy are equally likely. Thus the probability for a given partitioning of the energy (given set of n_i) is equal to the number of configurations with that set of n_i. How many distinct configurations of the total system are there with a given set $(n_1, n_2, \cdots n_N)$? This is a combinatoric problem that we will leave to you. The answer is

$$\frac{N!}{n_1! n_2! \cdots n_N!} = \frac{N!}{\prod_i n_i!} \tag{2.3}$$

The important point is that when N and n become large, subject to the constraints (2.1) and (2.2), the quantity in (2.3) becomes very sharply peaked around some set of

occupation numbers as in Figure 3 . Before we compute the occupation numbers that
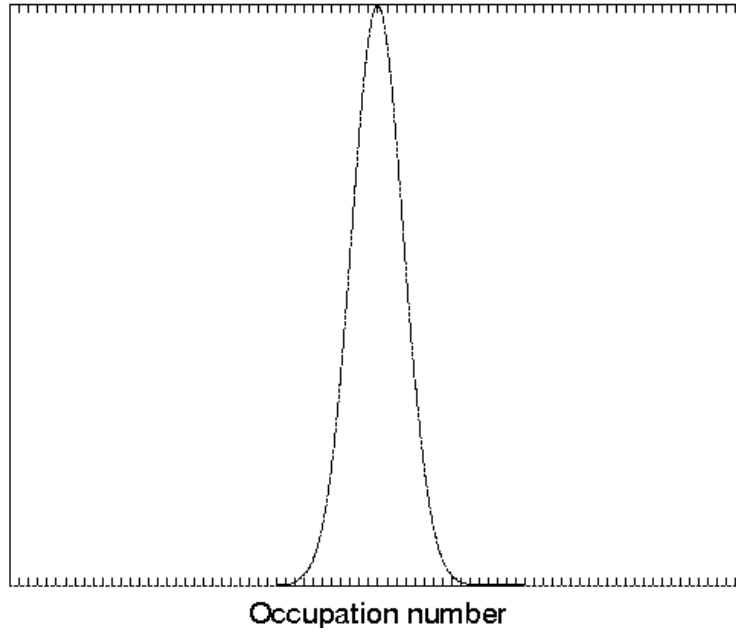
Figure 3: Sharply peaked occupation numbers.

maximize (2.3), let us introduce some changes of notation.

Define $P(i)$ to be the fraction of copies in state i.

$$P(i) = \frac{n_i}{N}$$

and let E be the average energy of a copy. Obviously

$$E = \frac{E_{\text{total}}}{N}.$$

Now (2.1) and (2.2) take a form identical to (1.2) and (1.3), namely

$$\sum_i P(i) = 1$$

and

$$\sum_i P(i)E_i = E.$$

Now we will assume that N and n_i are very large and use Stirling's approximation[¶] in (2.3). But first let us take its logarithm. (Maximizing a positive quantity is the same as maximizing its log.)

$$\log \frac{N!}{\prod_i n_i!} \approx N \log N - \sum_i n_i \log n_i.$$

We want to maximize this subject to the constraints (2.1) and (2.2).

Substituting $n/N = P$ and $E_{\text{total}} = NE$ we find that this is equivalent to maximizing

$$-\sum_i P(i) \log P(i)$$

subject to

$$\sum_i P(i) = 1$$

and

$$\sum_i P(i) E_i = E.$$

In other words the probability distribution for thermal equilibrium maximizes the entropy subject to the constraint of a given average energy.

In order to find an expression for $P(i)$ that provides a constrained maximum entropy value, we use the method of Lagrange multipliers (Appendix A). We introduce two multipliers α and β, one for each constraint. We maximize

$$-\sum_i P(i) \left[\log P(i) - 1\right] - \alpha \sum_i -E_{\text{total}} P(i) - \beta \sum_i P(i) E_i \tag{2.4}$$

At the end we find α, β values that satisfy the constraints.

Differentiating with respect to $P(i)$ and setting the result to zero gives

$$P(i) = e^{-(\alpha+1)} e^{-\beta E_i}. \tag{2.5}$$

This is the Boltzmann distribution.

Let us define

$$Z \equiv e^{(\alpha+1)}$$

Then (2.5) has the familiar form

$$P(i) = \frac{e^{-\beta E_i}}{Z}. \tag{2.6}$$

[¶]Stirling's approximation is $n! \approx n^n e^{-n}$ or $n \log n! \approx \log n - n = n(\log n - 1)$.

2.1 Solving for the Lagrange Multipliers

Solving for α is equivalent to solving for Z which is done by setting the sum of the P to 1. This gives the famous formula for the partition function,

$$Z = \sum_i e^{-\beta E_i}. \tag{2.7}$$

The partition function is a generating function that is used to derive several useful quantities, like a potential function. Numerical values of Z are generally not useful.

Next consider the equation

$$\sum_i P(i)E_i = E$$

which becomes

$$\frac{1}{Z} \sum_i e^{-\beta E_i} E_i = E.$$

Let us use $e^{-\beta E_i} E_i = -\partial_\beta e^{-\beta E_i}$ and we obtain

$$E = -\frac{1}{Z}\partial_\beta Z = -\frac{\partial \log Z}{\partial \beta}. \tag{2.8}$$

This equation can be used to fix β in terms of the average energy E.$^{\parallel}$

The Lagrange multiplier β is, of course, the inverse temperature. We will demonstrate this, but first let us derive another familiar thermodynamic formula.

2.2 Helmholtz Free Energy

Using $S = -\sum P \log P$ we can write the entropy in the form

$$S = \sum_i \frac{1}{Z} e^{-\beta E_i}(\beta E_i + \log Z) = \beta E + \log Z$$

The quantity $A = -T \log Z$ is called the *Helmholtz free energy* (reminder: $T = 1/\beta$.) Thus we find

$$S = -\beta(E - A)$$

or

$$A = E - TS \tag{2.9}$$

$^{\parallel}$The notation $\partial_x y$ is shorthand for $\partial y/\partial x$.

In its differential form,
$$dA = dE - TdS - SdT$$

Using $dE = TdS$ we find
$$dA = -SdT \qquad (2.10)$$

A is called free energy because it represents the amount of useful work that can be extracted from a system. The customary symbol A comes from the German *arbeit*, work.

2.3   Why is **T** $= 1/\beta$?

We have proposed two definitions of temperature. The first is equation (1.5) and the second is the inverse of the Lagrange multiplier β. We would like to see that they are really the same.

Consider a small change in the energy of a system,

$$dE = -d[\partial_\beta \log Z]$$

Now use (2.9) in the form $E = ST - T \log Z$ to get

$$dE = TdS + SdT - T\frac{d\log Z}{d\beta}d\beta - \log Z dT$$

Using (2.9) again, and the definition of A, we find that the last three terms cancel, leaving

$$dE = TdS. \qquad (2.11)$$

This is of course equivalent to (1.5) and thus the two definitions of temperature are the same.

2.4   Ensembles

For a closed system the energy does not fluctuate. In that case the probability distribution is a delta function of energy,[**]

$$P(E) = \delta(E - E_0)$$

[**]The Kronecker delta $\delta(x)$ is equal to one when $x = 0$ and zero otherwise.

This is called the *Microcanonical Ensemble* and governs the entire system including the heat bath.

For a system embedded in a large heat bath the energy fluctuates and the Boltzmann probability distribution is called the *Canonical Ensemble*. Later we will also allow the number of particles to fluctuate. The ensemble in that case is called the *Grand Canonical Ensemble*.

3   Fluctuations

Thus far we have been deriving classical thermodynamics from statistical mechanics. We go beyond thermodynamics when we consider fluctuations of quantities about their averages. Such fluctuations are observable – for example in Einstein's theory of the Brownian motion. In this section we will illustrate this by considering the fluctuations of the energy of a system in contact with a heat bath.

Given a probability distribution $P(x)$ the fluctuation in x (called Δx) is defined by

$$(\Delta x)^2 = \langle (x - \langle x \rangle) \rangle^2 \tag{3.1}$$

which is also equal to

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 \tag{3.2}$$

where $\langle X \rangle$ means the average value of X. For any function $f(x)$ the average is defined by $\langle f(x) \rangle = \sum_x f(x) P(x)$. If x is continuous then the sum is replaced by an integral in the obvious way.

Let us consider the fluctuation of energy of a system in equilibrium. We use the following:

$$\langle E \rangle = -\frac{1}{Z} \partial_\beta Z$$

and

$$\langle E^2 \rangle = \frac{1}{Z} \partial_\beta^2 Z.$$

The first identity is the usual identification of average energy in terms of the derivative of Z. The second identity is derived the same way as the first, noting that each derivative of $e^{(-\beta E)}$ brings down a factor of $-E$. Thus

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2$$

is given by

$$(\Delta E)^2 = \frac{1}{Z} \partial_\beta^2 Z - \left(\frac{1}{Z} \partial_\beta Z \right)^2.$$

But this expression is equivalent to

$$(\Delta E)^2 = \partial_\beta^2 \log Z = -\partial_\beta E$$

Using $T = 1/\beta$ we get

$$(\Delta E)^2 = T^2 \frac{dE}{dT}.$$

Now note that dE/dT is just the heat capacity of the system. Call it C. The final identity is

$$(\Delta E)^2 = T^2 C. \tag{3.3}$$

Thus we find that the fluctuation of the energy is proportional to the specific heat.

It may seem odd that the fluctuations should appear to be so large. But that is because we have set the Boltzmann constant to 1. If we put k back into the equation it becomes

$$(\Delta E)^2 = kT^2 C. \tag{3.4}$$

k is a very small number in units of meters, kilograms, seconds, and degrees Kelvin: $k = 1.4 \times 10^{-23}$. For a kilogram of water at room temperature,

$$\Delta E = \sqrt{1.4 \times 10^{-23} \text{J/K} \times (293K)^2 \times 4.18 J/(kg \times K) \times 1\text{kg}} = 2.2 \times 10^{-9} J$$

which is a very small amount of energy. Despite their small magnitude, however, fluctuations can be measured and in fact such measurements provide a method for determining Boltzmann's constant.

4 Control Parameters

So far we have considered closed systems characterized by constant values of the parameters in the Lagrangian such as the masses of particles, the values of external electric and magnetic fields, and the shape and volume of the containers that enclose the system. Some of these parameters such as the volume of the system and the external fields may be controllable from the outside, for example by moving pistons to change the volume. We will call such macroscopic control variables X_m. For simplicity we will consider the case of only one X although the principles are the same for several of them. If you want to think of a specific example, X can represent the volume of the system.

4.1 The Adiabatic Theorem and the First Law

An adiabatic process[*] means two things. First, the system is isolated so that no energy in the form of heat can flow into or out of the system. Secondly, it means that the control parameters are varied very slowly. In that situation the system will remain in equilibrium throughout the process, although typically the energy and temperature will change. Those things which do not change during an adiabatic process are called adiabatic invariants. It is a theorem that entropy is an adiabatic invariant. This theorem is true in classical mechanics but it is most easily understood in quantum mechanics.

Consider the energy levels of the system E_i. In general they will depend on X: $E_i = E_i(X)$. If a sudden change is made in X the system will not remain in an eigenstate of energy.[†] But if the change is arbitrarily slow then the adiabatic theorem says that the system remains in an eigenstate, simply tracking the slow time dependence of the instantaneous energy levels. In fact the levels will not cross over or disappear. The implication is that the probability function $P(i)$ is constant for each level, even as the energy along the way gradually varies. Obviously if $P(i)$ is constant, so is the entropy. That is why entropy is an adiabatic invariant.

Now consider the change in energy of the system during the adiabatic process. That energy change, is by definition, the work done on the system by changing X. The most familiar example is the work done in slowly compressing a gas in a insulated container.

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[*] "Adiabatic" is from the Greek "impassable."

[†] A system is in an eigenstate if it is undergoing periodic motion free of any external disturbances.

If the change in X is small (call it dX) we may assume the work done is small (call it dW). We can express this idea in equations.

$$dW = \left.\frac{\partial E}{\partial X}\right|_S dX$$

In the general case of several control parameters this becomes

$$dW = \sum_n \left.\frac{\partial E}{\partial X_n}\right|_S dX_n.$$

Let us define variables Y_n that are *conjugate* to to the X_n by the formula

$$Y_n = -\left.\frac{\partial E}{\partial X_n}\right|_S \tag{4.1}$$

and it follows that

$$dW = -\sum_n Y_n dX_n \tag{4.2}$$

The most familiar example of conjugate variables (X, Y) are volume and pressure (V, P).

$$dW = -PdV$$

Let us suppose that an infinitesimal adiabatic change is followed by a second process in which energy is added to the system in the form of heat – in other words, a second process in which the control parameters are constant but the entropy changes (just the reverse of what happened in the first process). For this second process $dE = TdS$ so that the combined effect of the work (adiabatic process) and the added heat give a change in energy,

$$dE = TdS - PdV$$

More generally

$$dE = TdS - \sum Y_n dX_n \tag{4.3}$$

This relation is called the *First Law of Thermodynamics*, but it is really an expression of energy conservation. The term TdS (energy due to a change of entropy) is called *heat* and is sometimes denoted dQ. But there is no function Q, and therefore, technically, dQ is not an exact differential. To see this we write (4.3) in the form

$$dQ = dE + YdX.$$

If Q were a well defined function of E and X then

$$\frac{\partial Q}{\partial E} = 1$$

and

$$\frac{\partial Q}{\partial X} = Y$$

would both hold true.

Consider $\partial^2 Q/\partial X \partial E$. Since the order of differentiation should not matter, one finds $(\partial Y/\partial E)|_X = 0$. For example one would find that the pressure would not depend on the energy of a gas with fixed volume. This of course is false, so dQ cannot be an exact differential.

The meaning of all of this is that it is possible to bring a system through a series of changes that bring it back to its original equilibrium state in such a way that the net input of heat is not zero. What must be zero for such a cycle is the change in the energy. In other words

$$\oint (dQ + dW)$$

must be zero.

4.2   Processes at Fixed Temperature

We have defined the conjugate variables Y such as pressure in terms of adiabatic or constant entropy processes. We can also define them in terms of constant temperature processes (isothermal). Such processes usually mean that the system is in contact with a heat bath which is so big that its temperature does not change during the process.

At this point we need a calculus theorem that we leave for you to prove. Suppose we have a function $S(T, X)$ of two variables T and X. Let there also be a second function $E(T, X)$. By solving for T in terms of S and X, we can think of E as a function of S and X.

.... Homework ....

Problem 4.1 Prove the following identity:

$$\left.\frac{\partial E}{\partial X}\right|_S = \left.\frac{\partial E}{\partial X}\right|_T - \left.\frac{\partial S}{\partial X}\right|_T \left.\frac{\partial E}{\partial S}\right|_X$$

This identity is general but in the case where S, T, E have their usual thermodynamic meaning, we can use

$$\left.\frac{\partial E}{\partial S}\right|_X = T$$

to get an expression for $Y \equiv -(\partial E/\partial X)_S$

$$\left.\frac{\partial E}{\partial X}\right|_S = \left.\frac{\partial E}{\partial X}\right|_T - T\left.\frac{\partial S}{\partial X}\right|_T = \left.\frac{\partial(E - TS)}{\partial X}\right|_T$$

Finally, using $E - TS = A$ this can be written $(\partial A/\partial X)|_T$. Thus,

$$Y = -\left.\frac{\partial A}{\partial X}\right|_T \tag{4.4}$$

Thus we can either define conjugate variables like pressure in terms of derivatives of E with respect to X at fixed entropy, *or* derivatives of A with respect to X at fixed temperature.

....

Part II

Some Simple Applications

5 Dilute Gas

In this section we study the properties of a dilute gas (as contrasted with very dense forms of matter such as Bose-Einstein condensate, which we study in Section 15. We begin with the well-known ideal gas, then add two-particle interactions. We then give molecules rotational inertia and finally study the van der Waals gas.

5.1 Ideal Gas

An ideal gas is defined as a system of non-interacting particles. Forces between particles due to collisions, electromagnetic fields, etc. are ignored.

Consider a container of volume V containing N identical non-interacting point particles, each with mass m. In order to apply the reasoning of Part I we must know how to define the state of the system and how to sum over states. Begin with a single particle.

The state of a classical system is described by a point in its phase space,[*] i.e., a value for each generalized coordinate and each generalized momentum. Thus in the present case we have a value for each of $3N$ coordinates whose values are restricted to the interior of the container, plus $3N$ momenta whose values are unrestricted.

To sum over states we imagine replacing the phase space by a discrete collection of small cells. The phase-space "volume" of each cell (units of momentum times length to the power $3N$) would tend to zero at the end of a classical calculation. But quantum mechanics suggests that we take it to be $(\hbar)^{3N}$. Thus we replace the sum over states by

$$\sum_i \rightarrow \int \frac{dx^{3N} dp^{3N}}{(\hbar)^{3N}}$$

(where $\hbar \equiv h/2\pi$ and h is Planck's constant). The energy of a state at point x, p is

$$E(x, p) = \frac{1}{2m} \sum_{n=1}^{3N} p_n{}^2 \tag{5.1}$$

and the partition function is

$$Z(\beta) = \frac{1}{N!} \int \frac{dx^{3N} dp^{3N}}{(\hbar)^{3N}} e^{-\beta E(x,p)}. \tag{5.2}$$

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[*]See Appendix B for an introduction to the concept of phase space.

The factor $1/N!$ is put in to avoid over-counting configurations of identical particles. For example if there are two particles, there is no difference between the configuration

particle-one at point x, p; particle-two at x', p'

and the configuration

particle-two at point x, p; particle-one at x', p'.

Thus we divide by the number of equivalent configurations which in this case is 2 and in the general case is $N!$. We will use Stirling's approximation, $N! \approx N^N e^{-N}$, in evaluating the partition function.

The x integrals in (5.2) are trivial since the integrand does not depend on x. The integral gives V^{3N} and when combined with the $1/N!$ we get

$$\left(\frac{eV}{N}\right)^N$$

Since N/V is the particle density which we call ρ, these factors combine to give

$$\left(\frac{e}{\rho}\right)^N$$

Notice how the N and V dependence nicely combine to give an expression which only depends on the density which we will keep fixed as the number of particles tends to infinity.

The momentum integral in (5.2) is a Gaussian integral over $3N$ variables. In fact it is the $3N$ power of the one dimensional integral

$$\int dp \ \ e^{-\beta \frac{p^2}{2m}} = \sqrt{\frac{2m\pi}{\beta}}.$$

The final result for the partition function is

$$Z(\beta) = \left(\frac{e}{\rho}\right)^N \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}} \tag{5.3}$$

If we want to explicitly exhibit the dependence on volume we replace ρ by N/V.

$$Z(\beta) = \left(\frac{eV}{N}\right)^N \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}} \tag{5.4}$$

.... Homework ....

Problem 5.1 Given the partition function in (5.4), compute A, E, S, and P as functions of the temperature. Derive the energy per particle and the ideal gas law $P = \rho T$. What is the average speed (magnitude of velocity) of a particle?

Problem 5.2 On a PV diagram (pressure on one axis, volume on the other) what are the curves of constant temperature (isotherms) and constant entropy (adiabats)?

What is the relation between pressure and temperature at fixed entropy?

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5.2 Almost Ideal Gas

Now let us introduce interactions between particles. We consider only potential energy due to interactions between pairs of particles. (More complicated 3-body, 4-body, $\cdots$ potentials are possible but we will ignore them).

$$U(x_1, x_2, \cdots, x_N) = \sum_{m>n} U(x_m - x_n) \tag{5.5}$$

We will treat U as a small quantity and compute Z to a first-order approximation:

$$Z(\beta) = \frac{1}{N!} \int \frac{dx^{3N} dp^{3N}}{(\hbar)^{3N}} e^{-\beta E(x,p)}$$

where

$$E(x,p) = \sum_n \frac{p_n^2}{2m} + \sum_{m>n} U(x_m - x_n)$$

To linear order in U,

$$Z = \frac{1}{N!} \int d^{3N}x \; d^{3N}p \; e^{-\beta \sum \frac{p^2}{2m}} \left[1 - \beta \sum_{m>n} U(x_m - x_n) \right]$$

which becomes

$$\frac{V^N}{N!} \left(\frac{2m\pi}{\beta} \right)^{\frac{3N}{2}} - \beta \frac{V^{N-2}}{N!} \left(\frac{2m\pi}{\beta} \right)^{\frac{3N}{2}} \frac{N(N-1)}{2} \int dx dx' \, U(x - x')$$

Using $\int dx\, dx'\, U(x - x') = V \int dx\, U(x) \equiv V U_0$, approximating $N(N - 1)$ by N^2, and using Stirling's approximation, one finds

$$Z = \left(\frac{e}{\rho}\right)^N \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}} \left[1 - \frac{\beta N}{2}\rho U_0\right] \tag{5.6}$$

To calculate $\log Z$ we use the first-order Taylor series for $\log(1 - \epsilon)$, namely $\log(1 - \epsilon) \approx -\epsilon$.

$$\log Z = -N \log \rho - \frac{3N}{2} \log \beta - \frac{N\beta}{2}\rho U_0 \quad + \text{ const} \tag{5.7}$$

. . . . Homework . . . .

Problem 5.3 Given the partition function in (5.7), compute A, E, S, and P as functions of the temperature. Derive the energy per particle. Find the correction to the ideal gas law $P = \rho T + \cdots$. What is the average energy of a particle? On a PV diagram (pressure on one axis, volume on the other) what are the curves of constant temperature (isotherms) and constant entropy (adiabats)?

Problem 5.4 Calculate the $\log Z$ to the next order (second order) in U and find the next correction to the ideal gas law.

. . . .

5.3   Ideal Gas in a Potential Field

Consider a box of gas subject to an external potential. For example the box could be in a gravitational field so that every particle has a potential energy $U = mgy$ where y is the vertical direction. More generally $U = U(x)$. The value of the potential at every point can be thought of as a control parameter. In the general case we have a continuous infinity of control parameters. Ordinary derivatives are replaced by functional derivatives.

What is the conjugate to the potential at point x? If we adiabatically increase the potential a tiny bit in some region, every particle in that region will have its energy increased. So the change in energy is

$$\delta E = \int d^3x\, \rho(x)\delta U(x).$$

The variational derivative of E with respect to $U(x)$ is just $\rho(x)$. Thus the conjugate to $U(x)$ is $-\rho(x)$.

Now consider the partition function. It is the same as for the ideal gas except that the integral $\int d^3x$ which gave a factor of volume for each particle in that case now becomes

$$\int d^3x \ e^{-\beta U(x)}$$

and we get

$$Z(\beta) = \left(\int d^3x \ e^{-\beta U(x)} \right)^N \left(\frac{2m\pi}{\beta} \right)^{3N/2} \tag{5.8}$$

The entire dependence of the free energy on U will be in the term

$$-TN \log \left(\int d^3x \ e^{-\beta U(x)} \right)$$

If we want the density at point y we functionally differentiate this expression with respect to $U(y)$.

$$
\begin{aligned}
\rho(y) &= \frac{TN}{\int d^3x \ e^{-\beta U(x)}} \beta e^{-\beta U(y)} \\
&= \frac{N}{\int d^3x \ e^{-\beta U(x)}} e^{-\beta U(y)} \tag{5.9}
\end{aligned}
$$

The factor $N/\int d^3x \ e^{-\beta U(x)}$ is independent of position. It can be replaced by a normalization constant K determined by the fact that the integral of the density must equal the total number of particles in the box.

$$\rho(y) = K e^{-\beta U(y)}. \tag{5.10}$$

Thus, as we might expect, the particles are most dense where the potential is lowest. For a gravitational field the density as a function of height is proportional to

$$e^{-\beta mgy}.$$

5.4 Diatomic Molecular Gas

So far we have considered a gas composed of point particles. If the molecules of the gas have structure, they are capable of internal motion such as rotation and vibration. To illustrate this idea we will consider a gas composed of diatomic molecules modeled by

two particles with mass $m/2$ connected by a rigid massless rod of fixed length ℓ. The mass moment of inertia about its centroid is

$$I = 2 \times \frac{m}{2} \times \left(\frac{\ell}{2}\right)^2 = \frac{1}{4}m\ell^2$$

We can use m and I to represent any rigid molecule having extension in space and thus rotational energy.

The partition function will factorize into a translational part and an internal part. The translational energy of the molecule is $p^2/2m$ where p represents its linear momentum. In addition there is rotational energy which we can derive. Let's suppose the rod is oriented in space with angular coordinates u, v where $0 < u < \pi$ and $0 < v < 2\pi$. You can think of u as the polar angle, and v as the azimuthal angle within a hemisphere. The rotational kinetic energy is

$$E_{\rm rot} = \frac{I}{2}(\dot{u}^2 + \dot{v}^2 \sin^2 u) \tag{5.11}$$

The canonical momenta are

$$p_u = \frac{\dot{u}}{I},$$

$$p_v = \frac{\dot{v}}{I \sin^2 u}$$

and the energy (Hamiltonian) is

$$E_{\rm rot} = \frac{p_u^2}{2I} + \frac{p_v^2}{2I \sin^2 u} \tag{5.12}$$

The integral $\int d^3x \, d^3p \, e^{-\beta p^2/2m}$ (there is one such factor for each molecule) is the same as for the point particle. The internal factor for each molecule is

$$\int du \, dv \, dp_u \, dp_v \, e^{-\beta E_{\rm rot}}. \tag{5.13}$$

First do the momentum integrals and obtain

$$\frac{2I\pi}{\beta} \int du \, dv \sin u = \frac{4\pi I}{\beta}$$

The constant $4I\pi$ is of no importance and we can drop it. The important thing is that there is a factor $1/\beta$ for each molecule. This means that the partition function in (5.3) is changed by replacing $\beta^{-3N/2}$ by $\beta^{-5N/2}$. The effect is to change the energy per molecule

from $\frac{3}{2}T$ to $\frac{5}{2}T$. In general we get an additional energy of $\frac{1}{2}T$ for each internal degree of freedom of the molecule (such as relative motion of two masses on an elastic link).

This leads to a famous paradox: as the distance between the parts of the molecule tends to zero, one would expect the molecule's behavior to approach that of the point particle. But the internal energy we just derived does not depend on the particle's size. Without going into details, we simply note that the resolution of the paradox involves quantum mechanics.

.... Homework ....

Problem 5.5 Calculate the thermodynamic properties of the diatomic gas. In particular find the adiabats on the PV diagram. Generalize the result to the case of n internal degrees of freedom.

....

5.5   A Note about Volume and the van der Waals Gas

Consider the factor $V^N/N!$ in the ideal gas partition function. Using Stirling we can write this as

$$\left(\frac{V}{N}\right)^N$$

One way to interpret this is to say that each particle moves in a box of size V/N.

Now let us suppose each particle is not really a point but rather an impenetrable sphere of volume v (a "van der Waals gas"). In that case the volume over which the center of mass can move is smaller and of order $V/N - v$. The partition function contains the factor

$$\left(\frac{V}{N} - v\right)^N$$

If we combine the idea of an impenetrable spherical particle with the corrections due to a long range weak potential, equation (5.6) becomes

$$Z = \left(\frac{V}{N} - v\right)^N \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}} \left[1 - \frac{\beta N}{2}\rho U_0\right] \tag{5.14}$$

and the free energy is

$$A = \log Z = -N \log\left(\frac{V}{N} - v\right) - \frac{3N}{2}\log\beta - \frac{N\beta}{2}\frac{N}{V}U_0 \quad + \text{const} \tag{5.15}$$

Calculating the pressure and rearranging the equation gives the van der Waals equation,

$$(P - \frac{u_0}{2}\rho^2)(V - Nv) = NT \tag{5.16}$$

6 Simple Magnet and Magnetization

Consider a collection of N spins $\sigma_1, \sigma_2 \cdots \sigma_N$, each of which can be up or down along the z axis (we will use the notation σ to indicate the z component of spin). There is a magnetic field H oriented along z and the energy of each spin is $\sigma\mu H$. Note that in this case the magnetic field is a control parameter.

Let the number of up spins be n and the number of down spins be m where $n + m = N$. The energy of such a configuration is

$$E = (n - m)H\mu$$

and the number of such configurations is

$$\frac{N!}{n!m!} = \frac{N!}{n!(N-n)!}.$$

The partition function is

$$Z(\beta, H) = \sum_n \frac{N!}{n!(N-n)!} e^{-\beta(n-m)H\mu}.$$

We have written the partition function in terms of β and H in order to indicate its dependence on temperature and the magnetic field.

The sum is a binomial expansion and the result is

$$Z(\beta, H) = (e^{\beta H\mu} + e^{-\beta H\mu})^N = (2\cosh\beta H\mu)^N. \tag{6.1}$$

and the free energy A is

$$A(\beta, H) = NT \log(2\cosh\beta H\mu). \tag{6.2}$$

The conjugate variable to the control parameter H is the magnetization M:

$$M = -\left.\frac{\partial A}{\partial H}\right|_T. \tag{6.3}$$

Using (6.2), we find that (6.3) gives

$$M = -N\mu \tanh\beta H\mu.$$

.... Homework ....

Problem 6.1 Compute the energy and entropy of the simple magnet. Find the functional form of the energy in terms of entropy. Do you see anything strange?

Problem 6.2 Show that M is the average total magnetic moment of the assembly of spins.

....

6.1   Ising Model

The so-called *Ising magnet* is equivalent to the simple magnet we just studied. Think of a one dimensional line of $N+1$ spins, each interacting with its two nearest neighbors except for the end-spins which have only a single neighbor. The system is defined by its energy

$$E = -j \sum_{i=1}^{N} \sigma_i \sigma_{i+1}. \tag{6.4}$$

The constant j is the strength of interaction between neighboring spins. At this point we will not introduce an external field although we could, but that makes the problem harder. Note that we have chosen the sign so that for positive j the energy is minimum when the spins are aligned. This is the *ferromagnetic* case. The anti-ferromagnetic case is defined by choosing j to be negative.

The trick is to write the partition function as the sum of two terms. The first term contains all configurations in which spin-one is up. To calculate this term let's change variables. Define "dual" spin variables μ_i. (These $\mu's$ are not magnetic moments. There should be no confusion; μ without an index is a magnetic moment. With an index it is a dual spin variable.)

$$\mu_i = \sigma_i \sigma_{i+1}.$$

There are N μ_i-variables labeled $\mu_1, \mu_2, \mu_3, \cdots \mu_N$. They are all independent and determine the original spins by the transformation

$$\sigma_j = \prod_{i=1}^{j-1} \mu_i.$$

For example, in the sector with the first spin up,

$$\sigma_1 = 1$$
$$\sigma_2 = \mu_1$$
$$\sigma_3 = \mu_1\mu_2$$

and so on. Note also that the μ_i take on the values ± 1 just as do the original spins.

The partition function in this sector is given by

$$Z = \sum \exp\left(\beta j \sum \mu_i\right).$$

This is exactly the same as the earlier model with the following substitutions:

$$H\mu \to -j$$

$$\sigma_i \to \mu_i$$

Thus the partition function in this sector is

$$Z = (2\cosh\beta j)^N$$

Finally we have to add the sector with $\sigma_1 = -1$. But the entire problem is symmetric with respect to changing the sign of all the spins simultaneously. Therefore the contribution of the second sector is the same as the first, and we find

$$Z = 2(2\cosh\beta j)^N \tag{6.5}$$

.... Homework ....

Problem 6.3 Add a term to (6.4) corresponding to an external magnetic field. In other words replace (6.4) by

$$E = -j\sum_{i=1}^{N}\sigma_i\sigma_{i+1} + \sum_{i=1}^{N+1}\mu H\sigma_i. \tag{6.6}$$

Compute the magnetization to linear order in the magnetic field. Note what happens in the limits of small and large temperature. Can you explain the behavior?

....

7   The Maxwell Relations

Unlike heat,* the total energy of a system is a well defined function of the thermodynamic equilibrium state. This means it is a function of all the control variables and one other variable such as the temperature or the entropy. For simplicity we will work with a single control variable, the volume, and freeze all the others.

The equation

$$dE = TdS - PdV$$

suggests that we think of E as a function of S and V. We can then write

$$\frac{\partial E}{\partial S} = T$$

$$\frac{\partial E}{\partial V} = -P \tag{7.1}$$

Now from the fact that $\partial^2 E/\partial S \partial V = \partial^2 E/\partial V \partial S$ we derive the first *Maxwell Relation*.
.

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V \tag{7.2}$$

Figure 4 illustrates a thought experiment to confirm the first Maxwell Relation. On the left we have an insulated cylinder with a movable piston that can be used to change the volume. We slowly move the piston and change the volume by dV. On the right we have a heat-conducting box of fixed volume and at temperature T. We allow an amount of heat dQ into the box and the pressure changes by dP.

Equation (7.2) is a remarkable bit of magic. With very little input we derived the general fact that for all systems the change in temperature under an adiabatic volume change is the negative of the change in pressure when we add a bit of entropy at fixed volume. It is very general and applies to solids, liquids, gases, black body radiation and more.

We can derive additional relation by focusing on the Helmholz free energy $A = E - TS$:

$$dA = dE - TdS - SdT = (TdS - PdV) - TdS - SdT$$

or

$$dA = -SdT - PdV. \tag{7.3}$$

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*We saw on page 19 that heat Q does not have an exact differential.
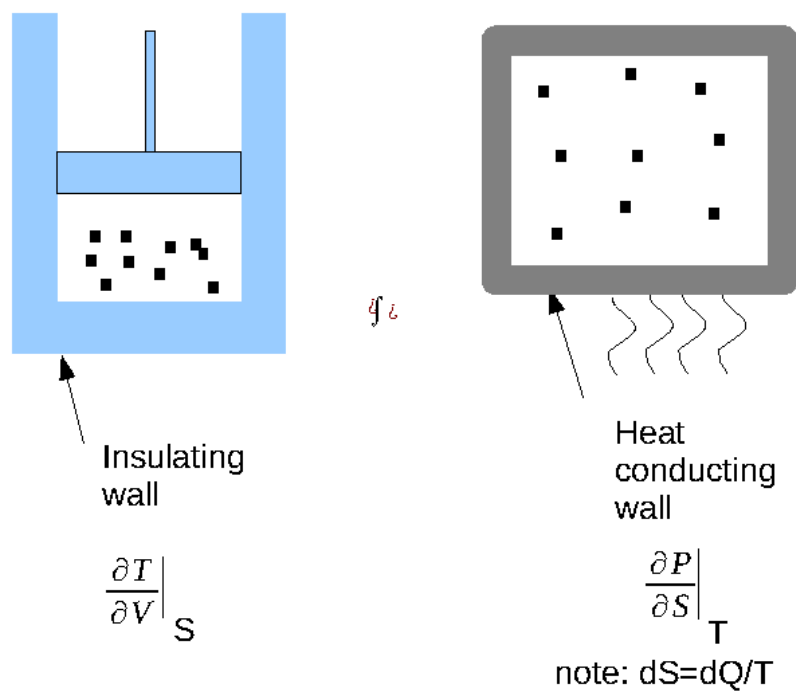
Figure 4: Experiment Illustrating First Maxwell Relation

We think of A as a function of T and V. Thus

$$\frac{\partial A}{\partial T} = -S$$

$$\frac{\partial A}{\partial V} = -P$$

and by using the fact that derivatives commute, we derive the second Maxwell relation.

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_S \tag{7.4}$$

The first Maxwell Relation follows from considering the energy as a function of the pair (S, V), and the second Maxwell Relation from $A(T, V)$. Two more relations can be obtained from functions $H(S, P)$ (enthalpy) and $G(P, T)$ (Gibbs free energy).

$$\begin{aligned} H &= E + PV \\ dH &= T\,dS + V\,dP \end{aligned} \tag{7.5}$$

Enthalpy is useful when considering a process at fixed pressure. For example, consider a gas in a cylinder with a piston such that the pressure is just the weight of the piston. The change in enthalpy if due to some added heat is just the heat added ($T\,dS$). If we call the heat added ΔQ, then $\Delta E + P\Delta V = \Delta Q$.

The corresponding Maxwell relation, the third, is

$$\left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P. \tag{7.6}$$

Finally the Gibbs free energy is defined by

$$\begin{aligned} G &= H - TS \\ dG &= V\,dP - S\,dT \end{aligned} \tag{7.7}$$

and the fourth Maxwell relation is

$$\left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T. \tag{7.8}$$

When using the Maxwell relations we can replace a differential change in entropy by dQ/T where dQ is the added heat energy.

.... Homework ....

Problem 7.1 Design experiments for confirming the second, third, and fourth Maxwell Relations similar to the one shown in Figure 4.

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8   The Second Law

Let us simplify the story a bit by considering an initial probability distribution on phase space which is constant over some small "blob" and zero outside the blob. In this case the entropy can be taken to be the logarithm of the phase space volume of the blob. In some sense it increases with time, but that seems to violate basic principles of mechanics.

The Second Law has an interesting history.* Boltzmann originally tried to define a quantity called H that always increased ($dH/dt \geq 0$) along a trajectory in phase space. But Loschmidt said that mechanics is reversible, so if H increases along a trajectory it will decrease along the time-reversed trajectory. Since the time-reversed trajectory is also a solution to Newton's equations, it is not possible to have a function on (p, x) that always increases.

The answer to this apparent paradox comes from chaos theory and coarse graining.

Chaos is the fact that for most systems the orbits in phase space are unstable. An example is a frictionless billiard system (ignoring the pockets). Start with the 15 numbered balls all arranged in a tight stack and carefully aim the Q-ball. If the initial conditions are perfectly reproducible then every time you do the experiment the result will be the same no matter how long you follow the orbits (the paths of the balls on the tabletop). But the tiniest error, either in the way the numbered balls are stacked, or in the initial trajectory of the Q-ball, will cause exponential growth, so that after just a couple of collisions the outcome will be extremely different.

This is a generic phenomenon in mechanics whenever there is more than one coordinate. It is characterized by a quantity called the *Lyapunov exponent*. Let the distance in phase space between two initial points be ϵ. After a small time the distance between them will be $e^{\lambda t}$ where λ is the (largest) Lyapunov exponent. It is easy to prove that the Lyapunov exponent must be greater than or equal to zero. Zero is a very exceptional value, implying no growth in ϵ, and for almost all systems with more than one degree of freedom, it is positive. Then the system is said to be chaotic.

To see what chaos implies, imagine following a patch of phase space – say at a fixed energy – as it evolves. The Liouville theorem† says that the volume and topology of the

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*See Appendix C.

†See, for example, the entry of that name at www.wikipedia.org.

region does not change, but in general the shape does change. If the system is chaotic, then points that were initially close will soon diverge. The shape branches out and forms a crazy fractal made of thinner and thinner tendrils spreading our over the phase space as in Figure 5. Eventually the tendrils will get arbitrarily close to any point on the energy surface of the initial points.

Suppose we take into account our inability to resolve points of phase space with arbitrary precision. In other words, we introduce a cutoff, replacing each phase space point by a small but finite sphere. We can coarse-grain the phase space blob by drawing such a sphere over each point in the original blob. Assuming the original blob is bigger than the cutoff, then at first, coarse graining has little effect. But as the tendrils spread the coarse-grained version fills a larger and larger volume, even thought the fine-grained blob has a fixed volume. Eventually the coarse-grained blob will fill the entire energy surface. Liouville's theorem does *not* tell us that the coarse-grained volume cannot increase. Of course the course-grained volume cannot be smaller than the fine-grained, so the coarse-grained volume cannot decrease.

Now come back to Loschmidt. After a long time imagine time reversing for every particle (this means reversing its momentum). If we do this for every point in the fine-grained blob, it will trace back to the original small round blob. Here is an example: take all the air in the room and start it out in a very small volume in the corner of the room. In a short amount of time the molecules will spread out over the volume and fill the room. Can the opposite happen? No, because this would violate the second law; the entropy of a confined gas is less than that of a gas that fills the room. But if we time-reverse every molecule of the final state, the air *will* rush back to the corner.

The problem is that if we make a tiny error in the motion of just a single molecule, that error will exponentially grow with the Lyapunov exponent and instead of lurking in one corner, it will traverse the entire room. We see that in the bottom of Figure 5. Some time-reversed trajectories (long lines) lead back to the original blob. Most don't, Even trajectories that start very close to one which does go back to the blob, quickly depart and go somewhere else. In fact if we run the coarse-grained blob backward in time (or forward) and then coarse grain the result, the phase space volume will be even bigger.

Freak accidents do happen, if you wait long enough. Given enough time the air in the room will by accident congregate in the corner. The correct statement is not that
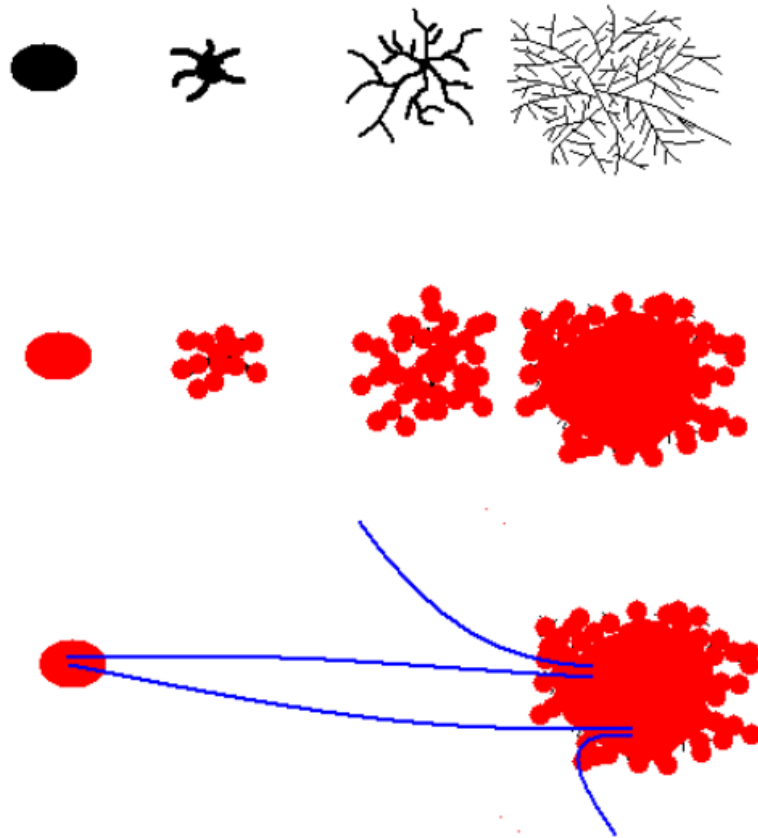
Figure 5: The Second Law. The phase space volume and topology are exactly conserved but when coarse grained it grows.

unlikely things never happen, but only that they rarely happen. The time that you would have to wait for this unusual air-event to take place is exponential in the number of molecules. So don't hold your breath!

Thus there are two kinds of entropies, fine-grained and coarse-grained. The fine-grained entropy never changes because of Liouville's theorem. The coarse-grained entropy does increase.

. . . . Homework . . . .

Problem 8.1 Suppose the room has volume of 100 cubic meters. Consider the possibility that all the air accidentally accumulates in a one cubic meter volume in the corner. What is the probability for this to happen? How long would you expect to have to wait to see it happen?

. . . .

9   Quantum Considerations

There are a number of paradoxes in statistical mechanics that were only resolved by the introduction of quantum mechanics. We saw one on p. 29. The energy per molecule of an ideal gas depends on the molecular structure: for point molecules it is $\frac{3}{2}T$ and for the diatomic molecule with fixed separation it is $\frac{5}{2}T$. But as the diatomic molecule gets smaller and smaller, it should tend to the point molecule. It does not, at least according to classical (non-quantum) statistical mechanics. Another example is the apparently infinite energy of black body radiation.

Let's begin with a simple example. Suppose there is a single harmonic oscillator (HO) in equilibrium with a heat bath. We can think of the HO as a molecule if we ignore its translational degrees of freedom. The Hamiltonian is

$$E = \frac{p^2}{2m} + \frac{kx^2}{2} \tag{9.1}$$

If we think of the HO as a molecule then p and x are *not* the position and momentum of the center of the center of gravity, but rather the relative variables. The mass m would be the reduced mass of the system. The partition function is

$$Z = \int dx\ dp\ e^{-\beta(p^2/2m + kx^2/2)}$$

or

$$Z = \int dp\ e^{-\beta(p^2/2m)}\ \int dx\ e^{-\beta(kx^2/2)}$$

The integrals are Gaussian, and using $\omega = \sqrt{k/m}$, give

$$Z = \sqrt{\frac{2m\pi}{\beta}}\ \sqrt{\frac{2\pi}{k\beta}} = \frac{2\pi}{\omega}\beta^{-1}. \tag{9.2}$$

An easy calculation gives the average energy of the oscillator to be

$$E = T. \tag{9.3}$$

Two things to notice about this energy: First, it is independent of m and especially of k. Second, in the molecular interpretation it is the internal energy of the molecule and would be added to the usual $\frac{3}{2}T$.

What is strange is that even in the limit of a rigid molecule ($k \to \infty$) the internal energy does not go away. One might have expected that when k is very large the molecule should be indistinguishable from a point molecule which has no internal energy.

Let us redo the calculation taking account of quantum mechanics. All we really need from QM is the fact that the energy spectrum is

$$E_n = \hbar\omega_n \tag{9.4}$$

where $n = 0, 1, 2, \cdots$ and $\omega = \sqrt{k/m}$, the oscillator frequency.

The partition function is

$$Z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}.$$

The sum is a geometric series:

$$Z = \frac{1}{1 - e^{-\beta\hbar\omega}} = \frac{e^{\beta\hbar\omega}}{e^{\beta\hbar\omega} - 1} \tag{9.5}$$

Finally, the average energy is

$$E = \frac{\omega\hbar}{e^{\beta\hbar\omega} - 1} \tag{9.6}$$

Note that at high temperature (small β) the answer agrees with the classical answer $E = T$. But for low temperature the energy is exponentially small:

$$E \approx \omega\hbar e^{-\omega\hbar/T}. \tag{9.7}$$

Notice that in the limit $k \to \infty$ (or equivalently $\omega \to \infty$) the energy of the oscillator goes to zero. In other words, the HO molecule *does* behave like the classical point particle which has no internal energy. Only when the temperature becomes large enough that the classical internal energy T becomes comparable to a single quantum does the molecule reveal its structure.

.... Homework ....

Problem 9.1 Compute the free energy and entropy of the classical and quantum oscillators. How do they compare for high and low temperature? Where is the transition from quantum to classical?

Problem 9.2 In section 5.4 the energy for the diatomic molecule could have been written

$$E = \frac{L^2}{2I}$$

In quantum mechanics L^2 takes on the values $n(n+1)\hbar$ and each energy level has degeneracy $2n+1$. The partition function for a single molecule can be written as an infinite sum over n. Estimate the sum in the limit of large and small temperature. Show that at high temperature the classical diatomic result is reproduced for the energy. Show that at low temperature the energy per particle tends to the point molecule limit.

....

10   Thermal Radiation

Consider a box (cube) with sides of length L. The walls of the box are reflecting. Electromagnetic radiation can exist in the box. The radiation can be decomposed into standing waves with the form

$$F(x, y, z) = \sum_{n_x, n_y, n_z} X(n_x, n_y, n_z) \, \sin \frac{n_x \pi}{L} x \, \sin \frac{n_y \pi}{L} y \, \sin \frac{n_z \pi}{L} z \qquad (10.1)$$

The dynamical degrees of freedom are the amplitudes $X(n_x, n_y, n_z)$ which behave like harmonic oscillators of frequency

$$\omega_n = \frac{n \pi c}{L} \qquad (10.2)$$

where $n \equiv \sqrt{n_x^2 + n_y^2 + n_z^2}$

The partition function is an infinite product of harmonic oscillator partition functions for each mode of oscillation. Classically

$$Z = \prod_{n_x, n_y, n_z} \frac{e^{\beta \hbar \omega_n}}{e^{\beta \hbar \omega_n} - 1}$$

Let us consider the energy of the system. Since $\log Z$ is a sum over the modes, the energy is just the sum of the energy of the oscillators. As we have seen, a classical oscillator has an energy equal to $T = \beta^{-1}$, independent of its frequency. Therefore each of an infinite number of modes has energy T and the total energy is infinite. Most of the energy is in very short wavelengths (large n) and the apparently infinite result is called the "Ultraviolet Catastrophe."

The resolution of the catastrophe is provided by quantum mechanics. As we have seen, the energy stored in a quantum oscillator is much smaller than the classical value when the frequency of the oscillator is large. Using (9.6) we find the total energy is the sum

$$E = \sum_{n_x, n_y, n_z} \frac{\omega_n \hbar}{e^{\beta \hbar \omega_n} - 1} \qquad (10.3)$$

which converges.

When the volume of the box is large the neighboring values of the ω_n are very close and the sum can be approximated as an integral. Let us define the wave vector k by $k_x = n_x \pi / L$ and similarly for y and z. The difference between neighboring wave vectors

is

$$\Delta k_x = \frac{\pi}{L}$$

and the sum is replaced by

$$\sum_{n_x, n_y, n_z} \rightarrow \frac{L^3}{\pi^3} \int d^3 k$$

We also note that $\omega_n = ck$ so that (10.3) becomes

$$E = \frac{L^3}{\pi^3} \int d^3 k \frac{ck\hbar}{e^{\beta \hbar ck} - 1}$$

multiplying by $T\beta = 1$ gives

$$E = \frac{L^3}{\pi^3} T \int d^3 k \frac{\beta ck\hbar}{e^{\beta \hbar ck} - 1}$$

Changing integration variables to $u = \beta \hbar ck$ we get

$$E = \frac{L^3}{(\pi c \hbar)^3} T^4 \int d^3 u \frac{|u|}{e^u - 1}$$

or

$$E = 4\pi \frac{L^3}{(\pi c \hbar)^3} T^4 \int_0^\infty du \frac{u^3}{e^u - 1}$$

The integral can be evaluated and gives a factor of $\pi^4/15$ leaving

$$E = \frac{4\pi^2}{15} \left(\frac{L}{c\hbar} \right)^3$$

We have done the calculation as if the field were a scalar with only one component. In fact the field has two components corresponding to the two possible polarizations. The net effect is that there are twice as many oscillators and the total energy is twice the above value.

.... Homework ....

Problem 10.1 Compute A, S, and P for thermal radiation. Work out all integrals.

....

11   Chemical Potential and Grand Canonical Ensemble

In the remainder of this text we are going to study three topics: magnets, the classical liquid-gas phase transition, and Bose-Einstein condensation. For all three applications we will need the concept of *chemical potential*.

The chemical potential is a useful tool for studying systems in which the number of particles fluctuates. Roughly speaking it is related to particle number in the same way that temperature is related to energy: as a Lagrange Multiplier.

Let's return to the derivation of the Boltzmann distribution (Section 2). Suppose there are some conserved quantities in addition to energy. For example suppose the system is a container of helium. The total number of helium atoms is conserved (assuming that the temperature is not high enough to break up the atoms).

There are situations in which the number of particles in each subsystem may fluctuate even though the total for all subsystems is fixed. For example, in considering the ensemble of N subsystems, we may allow helium atoms to be transferred from one subsystem to another. In that case only the total number of atoms is conserved. Suppose the number of atoms in the nth copy is called N_n. The constraint takes the form

$$\sum N_n = N_{\text{total}}.$$

A configuration of the (sub)system is now specified by an energy and a number of atoms, N, and the probability function depends on N as well as on the energy level. To implement the constraint of fixed N_{total} we introduce a new Lagrange multiplier. The Lagrange multiplier is $\beta\mu$ which includes a factor of β as a matter of custom. μ is called the *chemical potential*.

Following the same logic as in Section 2, it is easy to see that the probability function takes the so-called Grand Canonical form,

$$P(i, N) = Z^{-1} e^{-\beta(E_i + \mu N)}.$$

In this formula, the index i refers to the energy levels of the N-particle system and in general these levels will depend on N.

The partition function is defined so that the total probability is one. Thus

$$Z(\beta, \mu) = \sum_N e^{-\beta\mu N} Z_N \tag{11.1}$$

where Z_N is the partition function with fixed number of particles N.

Recall that in the case of energy, the Lagrange multiplier β is determined so as to fix the average energy. In the same way the chemical potential is determined to fix the average number of atoms. It is easy to see that

$$N = -\frac{\partial A}{\partial \mu} \tag{11.2}$$

where, as usual, $A = -T \log Z$.

Since $N = V\rho$ we can also think of the chemical potential as the parameter that allows us to vary the particle density.

.... Homework ....

Problem 11.1 Prove the following relations for processes at fixed volume and other control parameters:

$$
\begin{aligned}
E &= TS - \mu N - T \log Z \\
dE &= TdS - \mu dN
\end{aligned}
\tag{11.3}
$$

Problem 11.2 Find an expression for the fluctuation of the number of particles analogous to the relation in Section 3.

....

Let's calculate the Grand Canonical Partition function (GCPF) for an ideal gas. For a fixed number of particles the Canonical Partition function is

$$\frac{1}{N!} \left[V \left(\frac{2m\pi}{\beta} \right)^{3/2} \right]^N$$

The GCPF is gotten by multiplying this expression by $e^{-\beta \mu N}$ and summing over N. The result is

$$Z = e^{(2m\pi/\beta)^{3/2} V e^{-\beta \mu}} \tag{11.4}$$

and the free energy is

$$A = -T \log Z = -T \left(\frac{2m\pi}{\beta} V e^{-\beta \mu} \right) \tag{11.5}$$

.... Homework ....

Problem 11.3 Using (11.5), calculate the mean number of particles and the total energy as a function of the chemical potential. Then show that $E = 3N/T$.

....

12   Back to Magnets

Let's return to the Ising model in an external magnetic field and compute the magnetization to lowest order in the field. To simplify the notation we will set $\mu H = h$. We will mostly be interested in the ferromagnetic case with j being positive. In this case the energy is lowest when the spins line up in the same direction.

$$E = -j \sum_{i=1}^{N} \sigma_i \sigma_{i+1} + \sum_{i=1}^{N+1} h \sigma_i.$$

The magnetization M (eq. 6.3) is given in terms of the derivative of $\log Z$ with respect to h. For simplicity we replace (6.3) by

$$M = -\left(\frac{\partial A}{\partial h}\right) \tag{12.1}$$

To compute M to order h we must compute $\log Z$ to order h^2. Thus we write

$$Z = \sum_{\sigma} e^{\beta j \left(\sum_{i=1}^{N} \sigma_i \sigma_{i+1} - \sum_{i=1}^{N+1} h \sigma_i\right)}$$

and expand to order h^2.

$$Z = \sum_{\sigma} e^{\beta j \sum_{i=1}^{N} \sigma_i \sigma_{i+1}} \left(1 - \beta h \sum_i \sigma_i + \frac{1}{2}\beta^2 h^2 \sum_{i,j} \sigma_i \sigma_j\right) \tag{12.2}$$

It is easy to see that the term proportional to h vanishes. The original Ising model is symmetric with respect to changing the signs of all spins and that insures that only even powers of h survive. To order h^2 the logarithm of Z is given by

$$\log Z = \log Z_I + \frac{\beta^2 h^2}{2Z_I} \sum_{\sigma} e^{\beta j \sum_{i=1}^{N} \sigma_i \sigma_{i+1}} \sum_{i,j} \sigma_i \sigma_j. \tag{12.3}$$

where Z_I is the Ising partition function given by (6.5). For $i = j$ the term $\sigma_i \sigma_j = 1$. Thus we may write

$$\sum_{i,j} \sigma_i \sigma_j = N + 2 \sum_{i>j} \sigma_i \sigma_j$$

or

$$\sum_{i,j} \sigma_i \sigma_j = N + 2 \sum_{i,m} \sigma_i \sigma_{i+m}$$

where the m-sum starts at $m = 1$.

Now let us change to the dual variables $\mu_i = \sigma_i \sigma_{i+1}$. The term in (11.5) that is quadratic in h is given by

$$\frac{\beta^2 h^2}{2Z_I} \sum_\mu e^{-\beta j \sum \mu_i} \left(N + 2 \sum_{i,m} \sigma_i \sigma_{i+m} \right). \tag{12.4}$$

Now consider $\sigma_i \sigma_{i+m}$. In terms of the μ_i it is given by

$$\sigma_i \sigma_{i+m} = \mu_i \mu_{i+1} \mu_i \cdots \mu_{i+m-1}$$

Thus the second term in 12.4 gives

$$\frac{\beta^2 h^2}{(2 \cosh \beta j)^N} \sum_\mu e^{-\beta j \sum \mu_i} \left(\sum_{i,m} \mu_i \mu_{i+1} \cdots \mu_i \mu_{i+m-1} \right). \tag{12.5}$$

where we have replaced Z_I by the value we computed in Section 6. For those μ outside the range $(i, i + m - 1)$ the sum over the values of μ just cancel the corresponding factors of $(2 \cosh \beta j)$ in the denominator. For the points inside the range, the sum simply replaces $(2 \cosh \beta j)$ by $(2 \sinh \beta j)$. Thus the net result for large N is

$$N \beta^2 h^2 \sum_{m=1} (\tanh \beta j)^m = N \beta^2 h^2 \left(\frac{\tanh \beta j}{1 - \tanh \beta j} + \frac{1}{2} \right)$$

or more simply

$$N \frac{\beta^2 h^2}{2} e^{2\beta j}$$

The magnetization $(-\partial_h A)$ is

$$M = \beta h e^{2\beta j}. \tag{12.6}$$

First of all, notice that for all finite temperature the magnetization is linear and continuous in h for small h. This means that there is no spontaneous magnetization when h is shut off. But at zero temperature the coefficient $e^{2\beta j}$ diverges. The magnetization does not diverge at zero temperature but its derivative becomes infinite. At finite temperature the graph of M versus h looks like the solid line in Figure 6 while for zero temperature it looks like the dashed line. In other words, as you shut off the
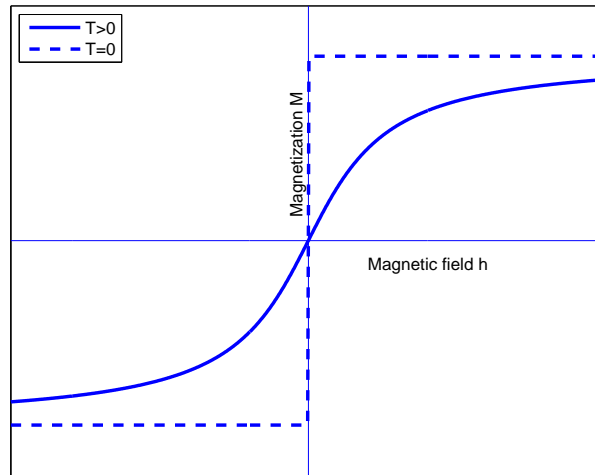
Figure 6: Magnetization vs external Magnetic field.

external field the magnetization persists, but this phenomenon only occurs at zero temperature for the Ising model. We will see that in higher dimensions the spontaneous magnetization persists up to a critical temperature.

The Ising model is characteristic of all one-dimensional statistical systems with short-range interactions. There is no phase transition at finite temperature.

Ising correctly solved the one-dimensional system and correctly told his advisor Lenz that it had no transition at finite T. His mistake was to conclude that the corresponding model in higher dimensions also had no transition.

12.1   Connection with Fluids

One of the interesting connections that we will explore is the connection between magnetic systems and the liquid-gas transition in molecular systems like water. Let us begin with a system of particles with 2-body potentials that consist of a hard core repulsion and a slightly longer range (but still short range) attraction. The hard core will be implicit in the configuration space integrations over position. No two particles will ever be allowed to be closer than some core size. The longer range potential, $U(x - y)$ will

be explicit.

Let the density of particles be ρ. The potential energy can be written in the compact form

$$\text{PE} = \int d^3x \, d^3y \, \rho(x)\rho(y)U(x-y). \tag{12.7}$$

Since the potential energy is independent of momentum and the kinetic energy is independent of position, the partition function factors into a position factor and a momentum factor $Z = Z_x Z_p$. The momentum factor give the usual $(2m/\beta)^{\frac{3N}{2}}$. It plays no role in determining the pressure or in the gas-liquid phase transition. We can ignore it for our present purposes. From now on we will just consider Z_x and drop the subscript x.

The partition function is

$$Z = \sum_{\substack{\text{config-}\\\text{urations}}} e^{-\beta \int d^3x \, d^3y \, \rho(x)\rho(y)U(x-y) - \beta\mu \int d^x \rho(x)} \tag{12.8}$$

Now imagine a lattice approximation to space (in any number of dimensions.) We will choose units in which the hard-core-size is unity. Thus, at each point in the lattice there may either be a particle or not, and no site may have more than one particle. If all sites are vacant we call the state the vacuum.

Let us introduce a variable at each point that indicates whether or not a particle is present. Call it σ_i where i indicates the site. If $\sigma = -1$ we say the site is vacant. If $\sigma = +1$ we say a particle occupies the site. In this way we map the problem of a system of identical molecules onto a magnetic system of the type we have studied.

If we work in units in which the lattice has unit spacing then the density is 1 on occupied sites and 0 on empty sites. Thus

$$\rho = \frac{1+\sigma}{2}$$

We also specify that the potential energy U is negative and that its range is one lattice spacing. In other words the potential is non-zero only for particles separated by a single link. Replacing integrals by sums, the energy is

$$\text{PE} = -4J \sum^{*} \rho(i)\rho(j) \tag{12.9}$$

where the symbol

$$\sum^{*}$$

means a sum over neighboring sites on the d-dimensional lattice. We take $J > 0$ so that if two particles are far apart the interaction energy is zero but if they are on neighboring sites the energy is negative. This corresponds to an attractive short range potential.

Using $\rho = \frac{1+\sigma}{2}$ we easily find

$$\text{PE} = -J\sum^{*} \sigma_i \sigma_j - 4J\sum_i \rho(i) + \text{ constant.}$$

From now on we drop the constant.

Let's add to the potential energy the chemical potential term $-\mu \sum_i \rho(i)$, which apart from a constant is $-\frac{1}{2}\mu \sum_i \sigma(i)$. The result is that the exponent in the expression for Z is

$$-J\sum^{*} \sigma_i \sigma_j - \left(4J + \frac{\mu}{2}\right)\sum_i \sigma(i) + \text{ constant.}$$

The partition function is the d-dimensional analog of the Ising model.

$$Z = \sum_\sigma e^{\beta\left(J\sum^{*} \sigma_i \sigma_j + \frac{8J-\mu}{2}\sum_i \sigma(i)\right)}$$

Obviously this is the d-dimensional analog of the Ising model in the presence of an external magnetic field $h = \frac{1}{2}(\mu - 8J)$.

Let us consider the magnetization M. It is simply the total number of sites times the average value of σ. Thus we may identify the magnetization per site (average of σ) as $2\rho - 1$.

Suppose a magnetic transition takes place so that at $h = 0$ there is a jump in magnetization. In the Ising model this only happens at $T = 0$ but in higher dimensions it happens at all temperatures up to some critical temperature T^* that depends on dimension. What does this jump mean from the point of view of the molecular system? It is a sudden jump in density as the chemical potential is varied. In fact it is the transition from a gaseous phase to a more dense liquid phase. The phase diagram is shown in Figure 7.

Notice that there are two ways to pass from one phase to another: cross the discontinuity (the thick line) or go around it. When you cross it the magnetization (density)
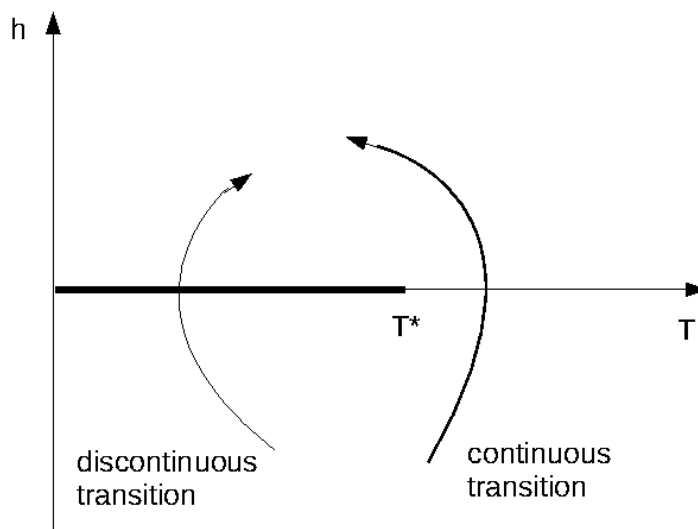
Figure 7: Phase diagram of a magnet. The thick line represents the discontinuity in the magnetization. In the 1-D Ising model the critical temperature T^* is zero. In the analogy with molecular fluids, negative magnetization represents the gas phase, and positive magnetization represents the liquid phase.

jumps in what is called a first-order transition. Going around the critical point involves no jump and the behavior is continuous. This is characteristic of both magnetic systems and gas-liquid systems such as water.

One interesting point is that in one dimension there is no gas-liquid phase transition.

12.2   Low Temperature Expansion

Something strange happens at zero temperature in the Ising model. To analyze it we can do a *low temperature expansion* (LTE). Actually the LTE is not an expansion in T but in $\exp\left(-2J\beta\right)$. Let's define the system by introducing extra dummy spins at the ends of the spin chain. We will take the number of "active" spins to be $N-1$ and add two more frozen "dummy" spins at the ends. These boundary dummy spins are assumed to be up $\sigma_{\text{dummy}} = +1$. The question is whether the boundary conditions are remembered far from the boundaries when $N \to \infty$.

Let us introduce new terminology: if two neighboring spins are the same we will say the bond between them is *unbroken*, which is the same thing as saying $\mu = 1$ for that bond. If neighboring spins are opposite ($\mu = -1$) the bond is *broken*. Note that there are N bonds including the bonds involving the dummy spins.

Each broken bond increases the energy by $2J$ and introduces a factor $\exp\left(-2J\beta\right)$ in the Boltzmann distribution. The LTE is an expansion in the number of broken bonds.

The first strange thing we see in the LTE is that free energy is not proportional to N. Since the boundary spins are frozen the number of broken bonds must be even. The LTE for Z has the form

$$Z = 1 + \frac{N(N-1)}{2} \exp\left(-4J\beta\right) + \cdots$$

and $\log Z$ is

$$\log Z = \frac{N(N-1)}{2} \exp\left(-4J\beta\right) + \cdots$$

The free energy seems to have a term proportional to N^2. This is odd because the free energy per site ($-T \log Z/N$) is not finite but rather is proportional to N.

In fact the free energy density does not have a term proportional to N. For every value of β it is finite. The point is that the things we are calculating in each order are the derivative of the free energy with respect to the expansion parameter. One way of saying this is that the first non-vanishing derivative of the free energy density is infinite

at $\exp(-2J\beta) = 0$. You can go back and check that from the exact solution. This is indicative of a singular behavior at $T = 0$.

Next consider the average value of a spin far from the boundary. At zero temperature the only state with non-vanishing probability has all the spins up. So every spin has average value $+1$.

For simplicity let's assume that N is even and that we focus on the spin at the center of the chain (just call it σ). There are $N/2$ bonds on either side of it. The average of σ is

$$\frac{1}{Z} = \sum e^{\beta J \sum \sigma_i \sigma_{i+1}} \sigma.$$

To leading order $Z^{-1} = 1 - \frac{N(N-1)}{2} \exp(-4J\beta) + \cdots$ To leading order (two broken bonds) the sum in the numerator has four types of terms. The first is a single term with no broken bonds. In the second, both broken bonds are to the left of σ. In the third term they are both to the right. In the fourth, one broken bond is on the left and one is on the right. The first term is 1.

For the second type of terms, $\sigma = +1$. We get

$$\sum_2 = \frac{\frac{N}{2}(\frac{N}{2} - 1)}{2} \exp(-4J\beta).$$

The third term – all broken bonds on the right – gives the same thing.

$$\sum_3 = \frac{\frac{N}{2}(\frac{N}{2} - 1)}{2} \exp(-4J\beta).$$

For the fourth type of terms $\sigma = -1$ and we get

$$\sum_4 = -\left(\frac{N}{2}\right)^2 \exp(-4J\beta)$$

Altogether we find that the average of σ to order $\exp(-4J\beta)$ is given by

$$1 - \left(\frac{N^2}{2} + \sum_2 + \sum_3 + \sum_4\right) \exp(-4J\beta) = 1 - \frac{N^2}{2} \exp(-4J\beta)$$

Again, the lesson is that the derivative of the magnetization with respect to the expansion parameter diverges (with a negative sign) as $N \to \infty$. What is going on is that the magnetization vanishes for all $T \neq 0$. The smallest temperature destabilizes the spontaneous magnetization, i.e., the effects of the infinitely distant boundary conditions.

The reason for this behavior is simple. In one dimension we can flip an arbitrary number of adjacent spins, breaking only two bonds, at a cost in energy which is only $4\beta j$. In other words a large block of flipped spins costs an amount of energy which does not grow with the size of the block.

12.3 Ising-like Systems in Higher Dimensions

In higher dimensions (number of dimensions $= d$) the situation is entirely different. To flip M spins you must break at least $\sim M^{1/d}$ bonds. This, of course, is a fact about the surface-to-volume ratio in d dimensions. Thus you pay a large energy price for flipping large blocks of spins. We will find that this stabilizes the low temperature behavior and implies that the spontaneous magnetization of the ground state does not disappear at finite T.

For definiteness let's take a square grid of lattice points with a total of n active spins. In addition there are dummy spins at the boundary that are chosen to be up as in Figure 8.
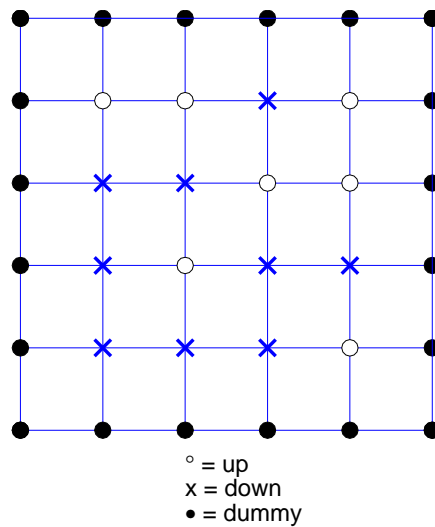

Figure 8: 2-dimensional lattice of spins. The o's indicate up-spins, the x's indicate down spins and the •'s indicate dummy up spins.

Some definitions for the 2-dimensional case:

- The spins are located on the *sites* of the lattice.

- The energy is a sum over pairs of nearest neighbor (NN) spins. NN pairs are associated with the *links* of the lattice.

- The squares of the lattice are called *plaquettes*. If you put a dot at the center of each plaquette they form the *dual lattice*. The links of the dual lattice are in one-to-one correspondence with the links of the original lattice. They cross the links of the original lattice at right angles.

The energy is given by

$$E = -J \sum_{}^{*} \sigma_i \sigma_j$$

where the sum is over nearest neighbors. We can also think of the energy as residing on the links of the lattice. The symbol

$$\sum_{}^{*}$$

can be understood as the *sum over links.* If there were no dummy spins the ground state would be 2-fold degenerate, i.e., all up or all down. But the dummies break the degeneracy and the ground state is all up spins.

For notational simplicity we will take the case where all the boundary spins are dummies.

Now consider the low temperature expansion. At zero temperature all the spins are up and the partition function is $Z = 1$. The first correction comes from flipping a single spin. This breaks four bonds on the links connected to that spin. The contribution from single flipped spins is

$$Z = 1 + Ne^{-8\beta J} + \cdots$$

$$\log Z = Ne^{-8\beta J} + \cdots$$

Note that the free energy is extensive to this order.

Let's check what happens to the next order. We can flip two spins. There are two possibilities; the two spins can be nearest neighbors or not. If they are not nearest neighbors, eight bonds are broken and the added energy is $16j$. If they are nearest neighbors only six bonds are broken and the added energy is $12j$. The reason that only

six bonds are broken is that the bond on the link connecting the pair is unbroken if both spins are flipped.

So the next order in the expansion comes from nearest neighbors (NN) and is of order $\exp{(-12\beta J)}$. The number of NN pairs is $2N$ for large N.

$$Z = 1 + Ne^{-8\beta J} + 2Ne^{-12\beta J}$$

$$\log Z = N\left(e^{-8\beta J} + 2e^{-12\beta J}\right)$$

Note that the free energy is still extensive, i.e., $\sim N$. This seems obvious since the number of NN pairs is $\sim N$.

The non-trivial test happens when we study non-nearest-neighbor pairs. The number of such pairs is $N(N-5)/2$. To see that, begin by picking a site and flipping its spin. The number of sites which are nearest-neighbor is five: the site itself and the four NN. But we have to divide by two for the usual reason of not over-counting. Thus to order $e^{-16\beta J}$ we find,

$$Z = 1 + Ne^{-8\beta J} + \frac{N}{2}e^{-12\beta J} + \frac{N(N-5)}{2}e^{-16\beta J}.$$

This looks dangerous because of the quadratic term in N. However, even if $\log Z$ is linear in N, we expect Z to contain things of higher order. To calculate $\log Z$ we use the formula

$$\log{(1+x)} = x - \frac{x^2}{2} + \cdots + \frac{x^n}{n} + \cdots$$

and find that the quadratic term in N cancels. Thus we find

$$\log Z/N = e^{-8\beta J} + \frac{1}{2}e^{-12\beta J} - \frac{5}{2}e^{-16\beta J} + \cdots$$

There are a few more terms that contribute in order $e^{-16\beta J}$. These terms come from adjacent flipped spins which break eight bonds. The spins can be in a line or in an L-shape. The contributions are $2Ne^{-16\beta J}$ and $4Ne^{-16\beta J}$ respectively.

Unlike the 1-dimensional case there is nothing divergent in the power series coefficients of the free energy density. This suggests that there is nothing discontinuous about the behavior at $T = 0$.

We can check this by examining the behavior of the average value of a spin far from the boundary.

$$\langle \sigma \rangle = Z^{-1} \sum_{\sigma} e^{\beta J \sum^* \sigma_i \sigma_j} \, \sigma$$

Again we sum over the number of broken bonds. The lowest order comes from a single flipped spin. If the flipped spin is not σ, the contribution is the same as to the partition function. But if the flipped spin is σ, the sign is changed. Thus

$$\sum_\sigma e^{\beta J \sum^* \sigma_i \sigma_j} \sigma = 1 + (N-1)e^{-8\beta J} - e^{-8\beta J} = 1 + Ne^{-8\beta J} - 2e^{-8\beta J}$$

Now we have to multiply by $Z^{-1} = 1 + Ne^{-8\beta J}$. Expanding to order $e^{-8\beta J}$ we find

$$\langle \sigma \rangle = 1 - 2e^{-8\beta J}$$

.... Homework ....

Problem 12.1 Compute the average value of σ to order $e^{-16\beta J}$ and show that the power series coefficients are finite in the limit $N \to \infty$.

....

You may ask where we used the dummy spins. The only thing we used them for was to break the degeneracy of the ground state. We could do something else that is often more relevant for real magnets. Introduce an extremely small external field h so that each spin has an additional energy $h\sigma$. This will align the ground state. For $h < 0$ the spins will line up in the up position. The energy cost of flipping all the spins is $2Nh$. We can redo the calculations and then let $h \to 0$. The average of σ will have a limit, but at low temperature the limit will depend on whether you approach from positive of negative h.

This phenomenon of spontaneous magnetization is a special case of spontaneous symmetry breaking. The symmetry is defined by changing the sign of all spins, $\sigma_i \to -\sigma_i$. It is a kind of "persistence of memory" in which an external magnetic field will be remembered even when it is switched off or made arbitrarily small.

We can diagnose the system without explicitly breaking the symmetry by studying the response to an external field. If we don't break the symmetry then for every configuration we must also allow the configuration in which each spin is reversed. Since the two configurations have the same energy, it is evident that they have the same probability and the average of any spin must be zero. That is even true at zero temperature.

But there is a consequence of the spontaneous symmetry breaking. It is this: if we find a given spin to be up (down) then it is more likely that we will find any other spin

to be up (down). In itself that is not really surprising. But we might expect the bias to disappear as the distance between the two spins becomes arbitrarily large. However, if there is spontaneous magnetization or symmetry breaking, then the correlation between different spins does not fade with distance.

We can say it in a precise way in terms of correlation functions. Define the average value of the product of two spins $\langle \sigma_a \sigma_b \rangle$ where a, b are two lattice sites.

$$C(a,b) \equiv \langle \sigma_a \sigma_b \rangle = Z^{-1} \sum_{\sigma} e^{\beta J \sum^* \sigma_i \sigma_j} \; \sigma_a \sigma_b \qquad (12.10)$$

Ordinarily, the bias introduced by finding one spin up (down) fades with distance, which means that $C(a, b) \to 0$ as $|a - b| \to \infty$. We define spontaneous symmetry breaking to mean that the limit of $C(a, b)$ is non-zero as the separation goes to infinity.

Let us go back to the 1-dimensional case. Notice that the second term in equation 12.4 is nothing but $\beta^2 h^2 C(i, j)$. The calculation that followed showed that

$$C(a,b) = \tanh \beta J^m \qquad (12.11)$$

where m is the separation between a and b. For zero temperature $C(a, b) = 1$ but for $T \neq 0$ the correlation tends to zero exponentially with distance. But in higher dimensions C does not vanish at infinity, at least for a range of temperature defined by the radius of convergence of the LTE.

Let's calculate $C(a, b)$ to order $e^{-8\beta J}$ without introducing dummy spins at the boundary. In this case the partition function is twice the previous value because we must sum over the two starting points, i.e., all down or all up, and then start flipping spins. Thus to the order that we are working with,

$$Z = 2 + 2Ne^{-8\beta J} + \cdots \qquad (12.12)$$

Next we consider

$$\langle \sigma_a \sigma_b \rangle = Z^{-1} \sum_{\sigma} e^{\beta J \sum^* \sigma_i \sigma_j} \; \sigma_a \sigma_b \qquad (12.13)$$

Begin with the ground state with all spins up. The contribution to the sum in (12.13) is of course the same as for the partition function, namely 1. Next, keeping σ_a and σ_b up, let us flip any other spin. The contribution is

$$(N - 2)e^{-8\beta J}$$

Next we flip σ_a. This time the contribution has the opposite sign to what it would be in the partition function. Combining it with the term coming from flipping σ_b (but not σ_a) we get

$$1 + (N-4)e^{-8\beta J}. \tag{12.14}$$

Note that the term with both σ_b and σ_a flipped is higher order in the expansion parameter. But this is just the term that arises from configurations that started with all spins up. Since we have dropped the bias coming from the dummy spins, we must add the contribution that arises from the opposite starting point.

Altogether we find

$$\begin{aligned} C(a,b) &= Z^{-1}(1 + (N-4)e^{-8\beta J}) \\ &= 1 - 4e^{-8\beta J} \end{aligned} \tag{12.15}$$

Note that the result is independent of how far away the spins σ_b and σ_a are from one another as long as they are not at the same point. In fact we can consider the result (12.12) to be the limit of $C(a,b)$ as the separation goes to infinity.

In higher orders one finds that the correlation function continues to be finite at infinite separation. In fact the asymptotic limit is just the square of the average of a single spin, assuming the dummy spins are put back.

The phenomenon of correlations remaining finite at infinite separation is called long range order and it persists over a range of temperature from $T = 0$ to some critical temperature. In the next subsection we will see that it does not persist to arbitrarily high temperature.

12.4   High Temperature Expansion

Now we come to the high temperature limit. Begin with Z. High temperature means small (βJ). Therefore the high temperature expansion (HTE) is gotten by expanding $\exp(-\beta E)$ in powers of (βJ).

$$Z = \sum_\sigma \left(1 - (\beta J)E + \frac{1}{2}(\beta J)^2 E^2\right) + \cdots \tag{12.16}$$

The nth term in the expansion is

$$Z_n = \frac{1}{n!}(\beta J)^n \sum_\sigma \left(\sum_{}^{*}(\sigma_i \sigma_j)\right)^n. \tag{12.17}$$
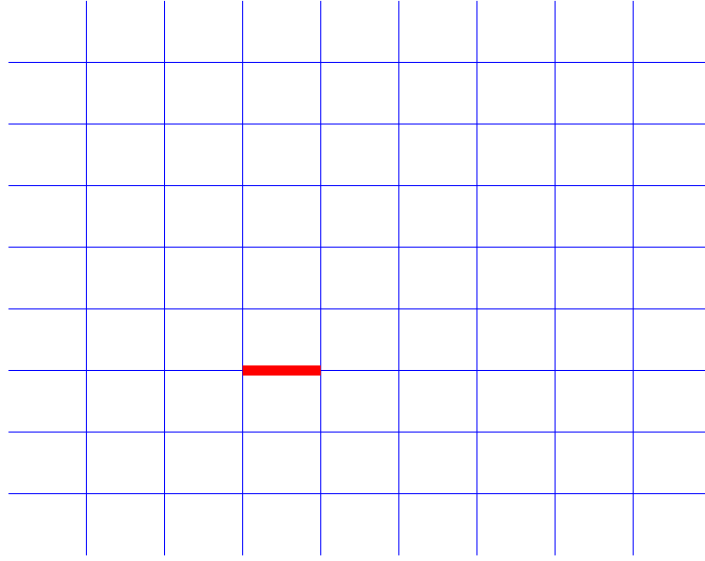
Figure 9: The contributions to the HTE coming from a single link are represented by a heavy line on that link.

Begin with the first term, $n = 0$. All states contribute equally and we get

$$
\begin{aligned}
Z_0 &= 2^N \\
\log Z &= N \log 2 + \cdots
\end{aligned}
\tag{12.18}
$$

Next, the $n = 1$ case. This involves a sum over nearest neighbors. Let us pick a link on the lattice and consider the pair connected by the link. We will represent the contribution of that link (connecting sites a, b) by drawing a line between sites as in Figure 9 It is given by

$$
2^{N-2}(\beta J) \sum_{\sigma_a, \sigma_b} \sigma_a \sigma_b = 2^N (\beta J) \frac{1}{4} \sum_{\sigma_a, \sigma_b} \sigma_a \sigma_b
\tag{12.19}
$$

This is obviously zero. The product $\sigma_a \sigma_b$ must average to zero because for each value of σ_a, the other spin, σ_b, can be 1 or -1. when summing, these will cancel.

Let's go to the next order involving two links. Suppose the two links are not the same. They could involve completely disjoint pairs or they may share one spin. In either case there will be spins to sum over which are occurring to the first power. Such sums vanish since the unmatched spin can be ± 1. But suppose the two links are the same. Then the term involves $(\sigma_a \sigma_b)^2$ which equals 1. The doubled links contribute. Their contribution is

$$2N(\beta J)^2 \tag{12.20}$$

The factor of $2N$ represents the number of links on the lattice. To see why the number of links is twice the number of sites draw a link to the right of every site and a link just below every site. As you range over all the sites you cover all the links. There are corrections but they are sub-leading in N.

The next non-vanishing contribution comes from 4-link terms. Odd number of links always leave unmatched spins so that when you sum over them the result vanishes.

The 4-link terms are of several types. For example, the four links can form a square, or two links can be covered twice. A single link can be covered four times. Among the cases in which two links are covered twice there are different possibilities depending on whether the links share a site. It would all be a lot easier if there were a rule that forbade a link from being covered more than once.

In fact we can rewrite the sum over configurations so that we never do cover a link more than once. Begin with the expression

$$Z = \sum_{\sigma} e^{\beta J \sum^* \sigma_i \sigma_j} \tag{12.21}$$

which is the same as

$$Z = \sum_{\sigma} \prod_{\text{links}} e^{\beta J \sigma_i \sigma_j}. \tag{12.22}$$

Now consider the expression $e^{\beta J \sigma_i \sigma_j}$. Since $\sigma_i \sigma_j$ can only take on the values ± 1 all even powers of $\sigma_i \sigma_j$ are equal to 1 and all odd powers are -1. By expanding the exponential and using this fact we find

$$
\begin{aligned}
e^{\beta J \sigma_i \sigma_j} &= \cosh \beta J + \sigma_i \sigma_j \sinh \beta J \\
&= \cosh \beta J (1 + \sigma_i \sigma_j \tanh \beta J).
\end{aligned}
\tag{12.23}
$$

Now we can write the partition function in the form

$$Z = (\cosh \beta J)^{2N} \sum_{\sigma} \prod_{\text{links}} (1 + \sigma_i \sigma_j \tanh \beta J). \tag{12.24}$$
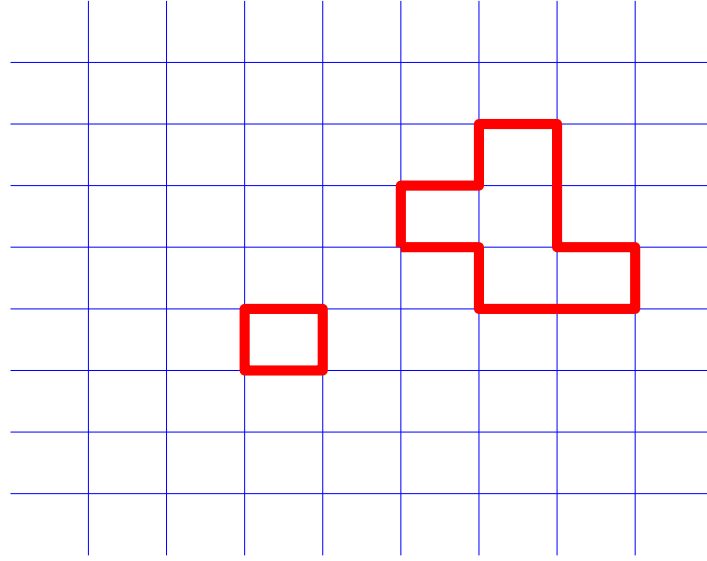
Figure 10: Closed "curves" on the lattice

When the product is expanded in powers of $\tanh \beta J$ we never cover the same link twice. For example at fourth order $(\tanh^4 \beta J)$ we get squares and nothing else. In fact at any given order we get one or more closed "curves" in which no link is multiply covered. Some examples are shown in Figure 10.

The partition function is given by

$$Z = (\cosh \beta J)^{2N} \sum_{\text{graphs}} C(\text{graph}) \tanh^m \beta J \qquad (12.25)$$

where the sum is taken over graphs consisting of any number of closed curves; $C(\text{graph})$ is a counting factor that enumerates the number of such graphs and m is the number of links that make up the curves.

. . . . Homework . . . .

Problem 12.2 Calculate the partition function, free energy, and average spin in both low and high T expansions for the case of the 3-dimensional Ising model. In the LTE

go to order $e^{-24\beta J}$. Show that the free energy is extensive and that the average magnetization is non-zero (zero) for low (high) enough temperature.

. . . .

12.5   One- and Two-Point Functions in the HTE

Now let's consider the averages $\langle \sigma \rangle$ (1-pt. function) and $\langle \sigma_a \sigma_b \rangle$ (2-pt. function) in the HTE.

It is obvious that the 1-pt. function vanishes to all orders in the HTE Boltzmann distribution in the form given in (12.24)

$$\prod_{\text{links}} (1 + \sigma_i \sigma_j \tanh \beta J). \tag{12.26}$$

when expanded to a given order in $\tanh \beta j$ involves an even number of spins. Multiplying by any odd number of spins and summing over the configurations will always give zero.

The 2-pt. function $C(a, b)$ is not zero. Computing it involves graphs with any number of closed curves and one open curve connecting the points a, b. The lowest order contribution comes from the shortest path connection them and has the value

$$C(a, b) = (\tanh \beta J)^n \tag{12.27}$$

where n is the number of links making up the shortest path. Thus we see an important generic feature of correlation functions at high temperature: they decay exponentially with distance. In this case it follows from the fact that $\tanh \beta J < 1$.

Since the asymptotic value of C at large separation satisfies $C(\infty) = 0$ for high temperature, and $C(\infty) \neq 0$ for low temperatures, there must be a value of temperature which separates the two regions. This point is the *critical point*.

. . . . Homework . . . .

Problem 12.3 Compute the 2-pt function to leading order in the HTE for 2 points on the same horizontal line and two points on the diagonal of a square. Extra Credit: Compute it to the next order?

. . . .
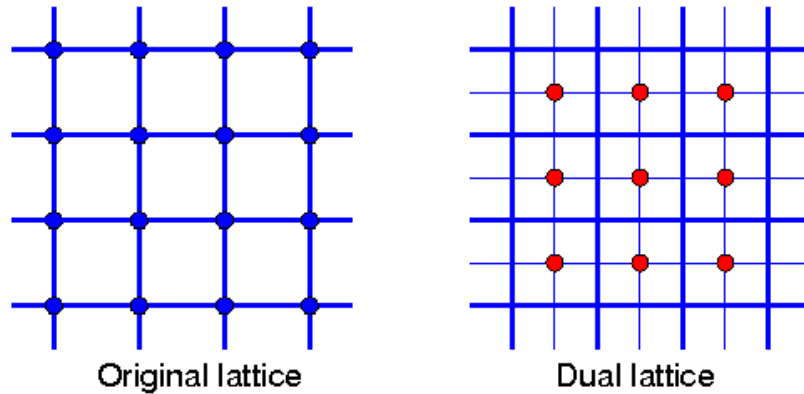
Figure 11: The dual lattice is composed of points at the centers of the Plaquettes.

13 High-T/Low-T Duality

The general properties of the Ising model in more than one dimension are independent of dimensionality. What is special about two dimensions is that the model can be exactly solved. We are not going to solve it but we are going to work out one special property that occurs in $d = 2$. It is called *duality* and it is rather easily seen from the LTE and HTE. We will focus on the partition function.

The HTE for Z is simple. We begin with the factor $(\cosh \beta J)^{2N}$. Then multiply this by a sum over all graphs involving any number of closed paths through the lattice. Assign each graph a weight given by $(\tanh \beta J)^n$ where n is the number of links in the graph. That's it.

Now consider the LTE for Z. Start with all spins up. Now flip a certain number. That breaks a certain number of bonds. For each broken bond include the factor $e^{-2\beta J}$. Sum over all such configurations.

The configurations of flipped spins can be enumerated in a clever way. Divide the flipped spins into disconnected islands and draw a closed curve around each island. To do that, it is convenient to define a dual lattice composed of the centers of all the plaquettes (Figure 11).

The closed curves surrounding the islands of flipped spins are composed of dual-

Figure 12: Surround each island of flipped spins with a curve on the dual lattice.

lattice links. In fact they have the same form on the dual lattice as the curves on the original lattice that were used to implement the HTE.

Each link on the dual curves is equivalent to a broken bond and the weight of such a configuration is $(\exp -2\beta J)^n$ where n is again the number of links forming the curves.

You may have realized by now that the LTE and HTE have exactly the same form except for two differences. First, in the HTE the partition function contains a factor of $(\cosh \beta J)^{2N}$ that has no analog in the LTE. Second, the LT expansion parameter is $\exp -2\beta J$ while the HTE parameter is $\tanh \beta J$. What this means is quite remarkable. Suppose we compute the partition function or the free energy as a function of $e^{2\beta J}$ from the LTE. Then we automatically know the behavior at high T. Just take $Z e^{2\beta J}$ and replace the argument of the function by $\tanh \beta J$. Then multiply by $(\cosh \beta J)^{2N}$ and you have the high temperature behavior.

If we assume that the critical point is the unique singularity on the T axis, it must lie at the symmetry point of the duality $\exp -2\beta j \leftrightarrow \tanh \beta j$. In other words the critical

point must be at $\exp -(2\beta J) = \tanh(\beta J)$ or equivalently the critical point is at

$$\sinh(2J\beta_{\text{crit}}) = 1. \tag{13.1}$$

Equivalently the critical temperature is

$$T_{\text{crit}} \approx 2.27J. \tag{13.2}$$

In higher dimensions the Ising model is dual to a theory living on the dual lattice but in general that dual theory is not the same as the original theory. For this reason the duality relates the critical temperatures of different theories rather than giving an equation for the critical temperature of the original theory.

There are many magical properties of the two-dimensional Ising model. We will show you one more. In summing over lattice curves (connected and disconnected) we must respect the rule that no link is covered more than once. Call this the "exclusion" rule. Suppose there were no such rule and that we could freely draw curves. Call the sum of all connected curves X. The sum of terms involving two disconnected curves would be $X^2/2$; three disconnected components, $X^3/3$. The sum would exponentiate to give $\exp X$, and the logarithm of Z would just be X. Since any connected component can be placed in N places, the free energy would be trivially seen to be extensive ($\sim N$).

In fact we can rearrange the sum so that there is no exclusion rule. Consider, for example, a diagram with two adjacent squares. This is forbidden by the exclusion rule. But let us combine it with a connected "figure-8" graph. The two are shown in Figure 13. Neither graph is allowed according to the exclusion rule, but there is another rule which allows such graphs but causes them to cancel. The rule is that every graph is to multiplied by a factor $(-1)^X$ where X is the number of times the graph crosses itself. With that rule the figure-8 graph cancels the graph with two adjacent squares. In fact the new rule is exactly equivalent to the exclusion rule and allows the sum of connected graphs to exponentiate. The rule can be used for the HTE directly, or for the LTE on the dual lattice. In Figure 11 another example is illustrated: the two connected graphs cancel leaving only the disconnected pair of squares with no overlapping links.

. . . . Homework . . . .

Problem 13.1 Use the new rules to calculate the $\log Z$ to order $(\tanh \beta J)^8$

. . . .

The new rule also applies to correlation functions such as $C(a,b)$.

Evidently the 2-D Ising model has some very simple features that make it exactly solvable but we will not get into the exact solution here.
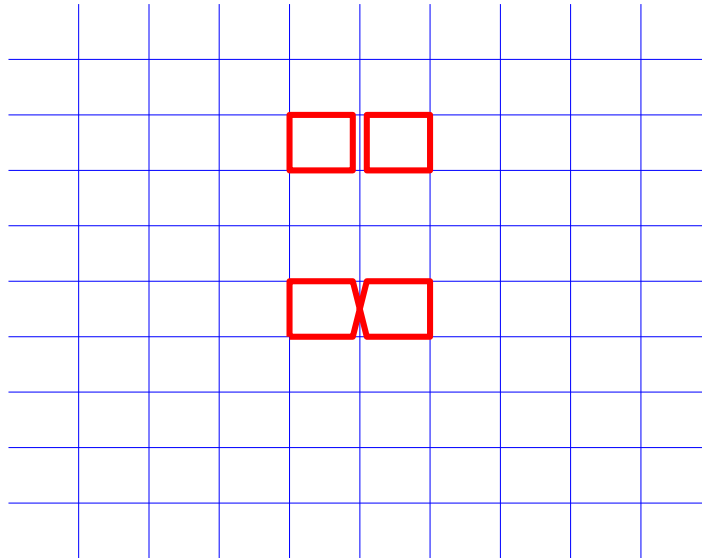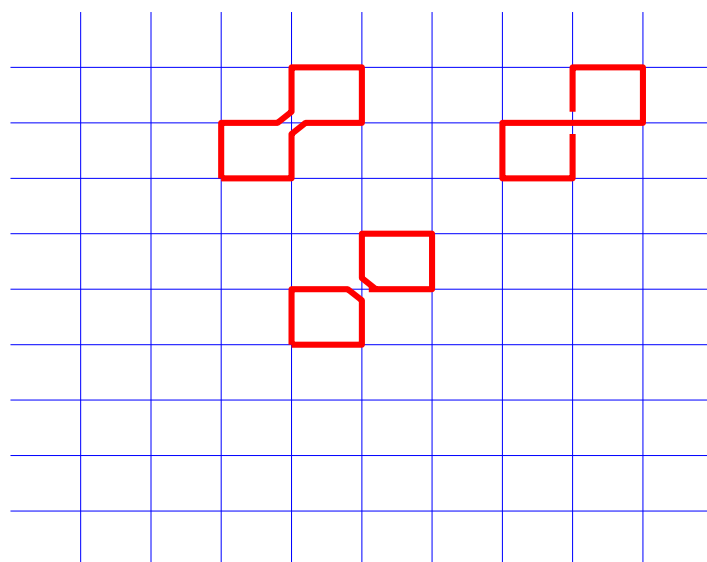

Figure 13: Two canceling graphs.

Figure 14: Another example.

14 What Happens at the Critical Temperature T_c?

The behavior of a system at its critical temperature depends on how that temperature is approached, i.e., from which direction in phase space. Let us begin by approaching the critical point from the high temperature side.

14.1 High Temperature Expansion of the Correlation Function

The high temperature behavior of the correlation function $C(a,b)$ exponentially falls to zero with distance. For simplicity we take the two points to be on the horizontal axis separated by D links. Let us also rename the expansion parameter by the simpler symbol X. Note $X < 1$.

To leading order $C(a,b)$ is given by

$$C(a,b) = (\tanh \beta J)^D + \cdots = X^D \tag{14.1}$$

Observe that at large separation the correlation function falls off exponentially.

$$\begin{aligned} C(a,b) &\sim e^{-mD} \\ m &= -\log X \end{aligned} \tag{14.2}$$

In general, for $T > T_c$ the correlation function exponentially tends to zero as with a decay parameter m that depends on temperature. In the high temperature limit $m = -\log(\tanh \beta J)$. The parameter m is the inverse to the "decay length" which is often called the *correlation length*.

To find the corrections to m we try a HTE for the logarithm of C.

The first correction involves graphs in which the line of links makes an extra little excursion with two additional links. The excursion can either be up one unit or down. There are $D(D+1)$ such graphs and they give

$$C(a,b) = \left[X^D \left(1 + D(D+1)X^2 \right) \right] \tag{14.3}$$

To compute the inverse correlation length m we take the log of C, divide by D, and let D tend to infinity. Taking the log of (14.3) to leading order in X gives

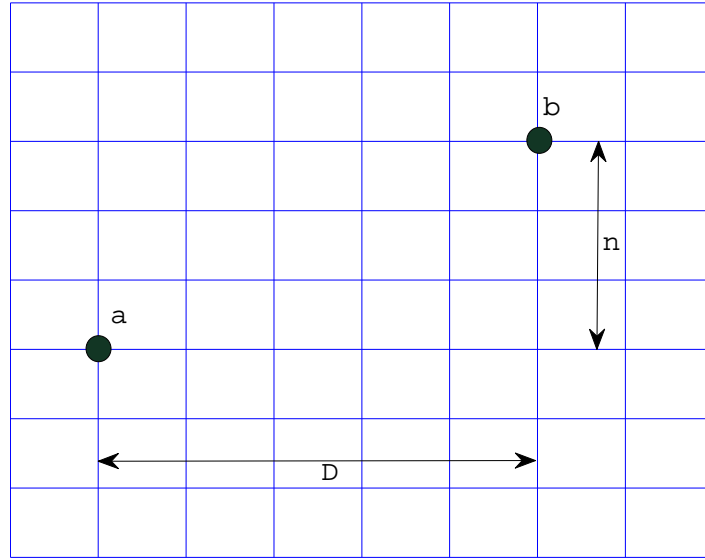$$\log C = D \log X + D(D+1)X^2 \tag{14.4}$$

Figure 15: Points a and b are separated along the x-axis by distance D and along the y-axis by distance n.

This is bad because when we divide by D the result grows like D and in the limit it diverges. The problem is that the correlation function does not exactly behave like an exponential of D. As we will see, there is a prefactor multiplying the exponential which gives $(1/D) \log C$ some extra non-analytic dependence on the expansion parameter.

To do the problem correctly we have to do it in "momentum space." Let us consider the two points a and b to be separated by D units along the x-axis and n units along the y axis, as in Figure 15.

Call the correlation function $C(D, n)$. Its Fourier transform* with respect to n is denoted $C(D, k)$. Suppressing the D dependence, standard Fourier analysis gives

$$C(n) \quad = \quad \frac{1}{2\pi} \int_{-\pi}^{+\pi} dk \, e^{-ikn} C(k)$$

---

*Appendix A

$$C(k) \;=\; \sum_{-\infty}^{+\infty} C(n) e^{ikn} \tag{14.5}$$

We will calculate $C(k)$ to order in X^2. All diagrams contain the factor X^D so let us ignore it for now. Later we will restore it. To order X^2 we can only get to $n = 0, \pm 1, \pm 2$. To get to larger values of $|n|$ requires more extra factors of X. Here is what we get.

$$
\begin{aligned}
C(0) &= 1 + D(D+1)X^2 \\
C(\pm 1) &= (D+1)X \\
C(\pm 2) &= (D+1)(D+2)X^2
\end{aligned}
\tag{14.6}
$$

and the Fourier transform $C(k)$ is given by

$$C(k) = 1 + 2(D+1)X \cos k + (D+1)^2 X^2 (1 + \cos 2k) - (D+1)X^2(1 - \cos 2k)$$

or, restoring the factor X^D and using the identity $1 + \cos 2k = 2\cos^2 k$,

$$C(k) = X^D \left\{ 1 + 2(D+1)X \cos k + 2(D+1)^2 X^2 \cos^2 k - (D+1)X^2(1 - \cos 2k) \right\} \tag{14.7}$$

Now take the logarithm. Note that there are no terms in $\log C(k)$ which are of order D^2. Dropping terms that are independent of D,

$$\log C(k) \approx 2DX \cos k - 2DX^2 \sin^2 k + D \log X \tag{14.8}$$

Now let us Fourier transform back to $C(0)$. From (14.5) we get

$$C(0) = X^D \frac{1}{2\pi} \int_{-\pi}^{\pi} dk \; e^{2DX \cos k - 2DX^2 \sin^2 k}. \tag{14.9}$$

For large D the integral is calculated by the method of stationary phase. We find the maximum value of the exponent with respect to the integration variable k and expand about it.

．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．． Homework ．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．．

Problem 14.1 Using stationary phase, show that the correlation function $C(D, 0)$ has the large D behavior

$$C \to \frac{1}{\sqrt{DX}} \left(X e^{2X} \right)^D$$

The prefactor $1/\sqrt{DX}$ is the problem in expanding $C(D, 0)$ directly in a HTE. But the Fourier transform is free of such non-analytic behavior.

．．

14.2 Approach to T_c

We have just seen that the inverse correlation length behaves like

$$m = |\log X| - 2X \tag{14.10}$$

In the high temperature limit m is infinite but as X increases the correlation length $1/m$ increases. The critical point T_c is the point at which $m(T)$ vanishes and the correlation length tends to infinity. Typically near the critical point $m(T)$ behaves like

$$m(T) \sim (T - T_c)^\nu \tag{14.11}$$

For temperatures lower than T_c the correlation function does not go to zero at large D. Right at T_C, C neither exponentially decays, nor is it non-vanishing at infinity. What does happen is that C falls to zero as a power of D. Thus at $T = T_c$ we write

$$C(a, b) = D^{-\eta} \tag{14.12}$$

The constants ν and η are called critical exponents. The constant η is often replaced by $\eta = 2\Delta$ where Δ is called the *dimension* of the "field" σ.

The general theory of the critical behavior is the *renormalization group* (RG). I will just touch on it and give the main idea.

14.3 Renormalization Group

For the moment forget that the spin σ can only take on the values ± 1. In place of σ we introduce a continuous variable f_i at each lattice site. Think of f as a field which ranges over the real numbers. Consider a function F of all the spins. It represents the integrand of the partition function, i.e., $F = \exp -\beta E(f)$. The partition function is given by

$$Z = \int \prod_i df_i \, F(f). \tag{14.13}$$

Next, let us coarse-grain the lattice by grouping four sites together and call the resulting 2×2 square a *supersite*. On each supersite define a variable f' (sometimes called a block variable).

$$f' = \frac{\lambda(f_1 + f_2 + f_3 + f_4)}{4} \tag{14.14}$$

where λ is a number to be chosen later.

Now let us carry out the sum in equation (14.9) in two steps. First integrate over the f_i holding fixed the values of f' on each supersite. That gives us a function

$$F'(f') \tag{14.15}$$

of all the block variables. The result is a new statistical mechanical problem on a lattice with twice the spacing as the original lattice and one quarter as many variables. In the infinite lattice limit we can just think of it as another problem on the exact same lattice but we will have to remember that physically, it has been re-scaled.

Consider the operation of going from the function F to the function F'. Let us call that operation $\mathcal{B}$.

$$\mathcal{B}F = F'. \tag{14.16}$$

If we think of F being determined by a set of parameters $\{g\}$ and F' by a similar set $\{g'\}$ then $\mathcal{B}$ just represents the functional dependence of g' on g. Schematically,

$$\begin{aligned}
g'_1 &= \mathcal{B}_1(g_1, g_2, g_3, \cdots) \\
g'_2 &= \mathcal{B}_2(g_1, g_2, g_3, \cdots) \\
g'_3 &= \mathcal{B}_3(g_1, g_2, g_3, \cdots) \\
&\vdots
\end{aligned} \tag{14.17}$$

Once we have the functions $\mathcal{B}$ we can iterate the process and thin the lattice by another factor of 2 in spacing. Thus we can consider a sequence of F functions – call them F_n – that all represent the same problem after n lattice doublings.

$$F_{n+1} = \mathcal{B}F_n. \tag{14.18}$$

In other words we have a recursion relation for F. If we have an initial starting point we may iterate the procedure and define a sequence of progressively coarse-grained versions of the problem. To complete the problem we need to specify in initial condition. For the Ising model the initial condition is

$$F(f) = \prod_i \delta(f_i^2 - 1)e^{\beta J \sum^* f_i f_j} \tag{14.19}$$

Critical points correspond to fixed points of $\mathcal{B}$, i.e., values of the parameters of F which reproduce themselves:

$$F_{fp} = \mathcal{B}F_{fp}. \tag{14.20}$$

Under certain conditions a given starting point may flow to the fixed point after many iterations of the RG transformation $\mathcal{B}$. That is what a critical point is; a starting point that flows to a fixed point.

Let us consider the behavior of the correlation function $C(D)$ at the fixed point. Consider a doubling of the lattice spacing. Obviously, since the problems are identical on the original and the doubled lattice we can expect

$$\langle f'(0)f'(D)\rangle = \langle f(0)f(D)\rangle \tag{14.21}$$

but we must remember that on the left side, D represents a physical distance twice as big as it does on the right side.

Rewriting (14.17) using

$$f' = \frac{\lambda(f_1 + f_2 + f_3 + f_4)}{4}$$

and the fact that for large D all the f_i in the supersite at the origin are separated from those in the supersite at D by distance $2D$ on the original lattice, we find

$$C(2D) = \lambda^{-2}C(D). \tag{14.22}$$

It follows that C varies as a power of D as in (14.8) and the critical exponent η satisfies

$$\eta = 2\log\lambda \tag{14.23}$$

or in terms of the dimension Δ

$$\Delta = \log\lambda \tag{14.24}$$

The implication of all of this is that at the critical point the physics is invariant with respect to re-scaling the lattice, as long as we re-scale the average (over the 4 sites in the supersite) by a factor of λ. Moreover it is determined by the recursion relation $\mathcal{B}$, not the exact starting point. After many iterations the exact initial state becomes irrelevant and the behavior tracks to the fixed point. For example, the critical behavior does not depend on whether there are second nearest neighbor interactions, or whether the original lattice is a square, triangular, hexagonal $\cdots$ lattice. In fact the long-distance behavior of the correlation function at T_c becomes isotropic (rotationally symmetric).

14.4   Mean Field Theory

Mean field theory is another type of approximation that is useful for approaching the critical point from the low temperature side. We have seen that the low T behavior involves spontaneous magnetization, or spontaneous symmetry breaking. The symmetry of the Ising model is the discrete reflection $\sigma \to -\sigma$. The magnetization is proportional to the average of σ and is non-zero even as the external field tends to zero. The quantity $s \equiv \langle \sigma \rangle$ is an example of an *order parameter*, i.e., a quantity which must be zero unless the symmetry of the system is spontaneously broken.

Mean field theory is an approximation whose validity depends on the dimension of the lattice: the higher the dimension d, the better the approximation. It becomes exact in the limit of high dimension, but it completely fails for $d = 1$. It is order-of-magnitude accurate for $d = 2$ and reasonably accurate for $d = 3$.

Let us begin by assuming that the order parameter is non-zero at temperature β^1. Let us focus on a given spin σ. It is surrounded by $2d$ neighbors which it interacts with through the usual interaction $-J\sigma\sigma_j$. If d is very large we can assume that the σ sees an average spin s for each of its neighbors. In other words the energy of the spin is

$$E = -2dJs\sigma. \tag{14.25}$$

It is also true that if the number of neighbors is large, the fluctuations about the average are small. Thus we can treat each spin as being in a mean field (mean in the sense of average) and calculate its average spin.

The partition function for the single spin is

$$Z = \sum_{\sigma} e^{2d\beta Js\sigma} = 2\cosh\left(2d\beta Js\right) \tag{14.26}$$

and the average of s obtained by differentiating $\log Z$ is

$$\langle \sigma \rangle = \tanh\left(2d\beta Js\right). \tag{14.27}$$

Consistency requires $\langle \sigma \rangle = s$, so we find an equation for the order parameter:

$$s = \tanh\left(2d\beta Js\right). \tag{14.28}$$

This equation is illustrated in Figure 16. The critical temperature is the value at which
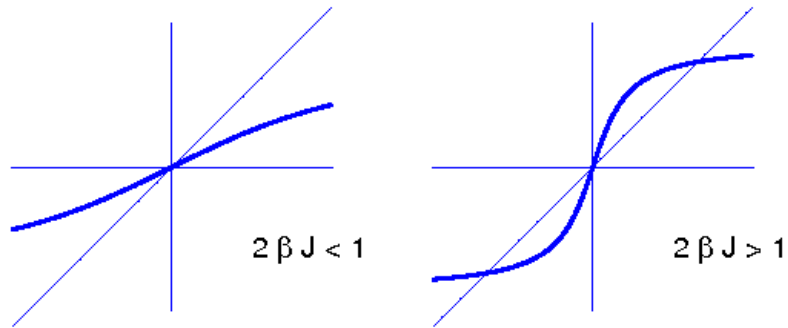
Figure 16: The mean field consistency relation at high T (left) and low T (right). For low T the tanh-curve and the linear curve intersect twice: once for positive s and once for negative s.

the slope of $\tanh(2d\beta Js)$ at $s = 0$ is unity. In other words

$$T_c = 2dJ \tag{14.29}$$

How good is the mean field method? For $d = 1$ it's very bad. It predicts a critical temperature $T_c = 2J$ where the true value is zero. For $d = 2$ it's better. Mean field theory gives $T_c = 4J$ and the exact solution gives $T_c = 2.27J$. MFT is even better in $d = 3$ where it gives $T_c = 6J$ compared to simulations that give $T_c = 4.6J$.

Problem 14.2 Here is a proposal for an improved mean field approximation. Instead of focusing on a single spin and treating it in the mean field background, focus on a nearest-neighbor pair in the MF background. Call the pair a and b. The energy of the pair in the MF is

$$E = -J\sigma_a\sigma_b - J(2d - 1)s(\sigma_a + \sigma_b)$$

Compute Z for the two-spin system and then compute the average value of σ_a. (The average of σ_b will be the same.)

By equating this average to s you will obtain a MF consistency condition. Use it to compute the critical temperature and compare it with the previous approximation.

....

Part III

Quantum Gases

15   Bose Einstein Condensation

We are going to study quantum gases, i.e., gases at low enough temperature that the quantum statistics of particles cannot be ignored. There are two kinds of particles in nature, bosons and fermions.[†] When the temperature of a gas is high a gas of fermions behaves the same way as a gas of bosons and both behave like a gas of classical particles. To see why, consider the average kinetic energy of a classical molecule at temperature T.

$$p^2/2M = (3T)/2$$

We can also say that the square of the uncertainty in the momentum of a particle is of order

$$(\Delta p)^2 \; = MT$$

From the uncertainty principle the spread in the wave function of a particle is at least

$$\frac{\hbar}{(MT)^{1/2}}$$

If this is much less than the spacing between particles, the wave functions of the particles don't overlap and are orthogonal. In this case the statistics does not matter. The distance between molecules is of order $\rho^{-\frac{1}{3}}$. Thus the behavior is classical if

$$\rho < \frac{(MT)^{3/2}}{\hbar^3.} \tag{15.1}$$

But for fixed density (15.1) will become violated at low enough temperature and the wave packets will overlap. Under those circumstances the fermionic or bosonic nature of the molecules becomes important.

In the case of bosons, the statistics favor particles being in the same state. The more particles in a given quantum state, the more likely it is that an additional particle will wind up in that state. From the Maxwell Boltzmann distribution, the most likely state for a particle is the state of lowest energy. In the bose gas at low temperature there will be a much larger number of molecules in the lowest energy state than in the classical gas.

[†]Bosons (photons, gluons, etc.) can occupy the same quantum states whereas fermions (electrons, protons, neutrons, etc.) cannot.

At this point it might be a good idea to go back and review the theory of black body radiation in Section 10. Photons are bosons and the same methods apply to ordinary bosonic molecules.

Non-relativistic bosons of mass M are described by a wave field Ψ that is analogous to the electromagnetic field although it has only a single (complex) component. The field can also be decomposed into oscillators. If the molecules are confined to a box of linear dimensions L the wave numbers satisfy

$$
\begin{aligned}
k_x &= \frac{\pi n_x}{L} \\[2mm]
k_y &= \frac{\pi n_y}{L} \\[2mm]
k_z &= \frac{\pi n_z}{L}
\end{aligned}
\tag{15.2}
$$

with n being integers.

The momentum of a particle is given by $p = \hbar k$ and the energy by

$$
E = \frac{p^2}{2M} = \frac{\hbar^2 k^2}{2M} = \frac{\hbar^2 \pi^2}{2ML^2} n^2.
\tag{15.3}
$$

The frequency of the oscillators is

$$
\omega_n = \frac{\hbar \pi^2}{2ML^2} n^2
\tag{15.4}
$$

Using the same method that we used for thermal radiation, the partition function is

$$
Z = \prod_n \left(1 - e^{-\beta \frac{\hbar^2 \pi^2}{2ML^2} n^2} \right)
$$

However, there is one feature of the non-relativistic gas not shared by a gas of photons. Non-relativistic molecules are conserved whereas photons are easily emitted and absorbed. In order to account for the conservation of molecules we must introduce a chemical potential. This is equivalent to shifting the energy of each particle by μ. The grand canonical partition function has the form

$$
Z = \prod_n \left(1 - e^{-\beta \frac{\hbar^2 \pi^2}{2ML^2} n^2 - \beta \mu} \right)^{-1}
\tag{15.5}
$$

The Helmholtz free energy is

$$A = -T \log Z = T \sum_n \log \left(1 - e^{-\beta \frac{\hbar^2 \pi^2}{2ML^2} n^2 - \beta\mu}\right) \tag{15.6}$$

The next step is to replace the sum by an integral. Let us first change variable from the integers n_i to u_i where

$$u_i = \frac{\hbar\pi}{\sqrt{2M}L} n_i$$

Note that the relation between sums and integrals is

$$\sum_n \rightarrow \left(\frac{\sqrt{2M}L}{\hbar\pi}\right)^3 \int d^3u$$

Thus the free energy becomes

$$A = T \left(\frac{\sqrt{2M}L}{\hbar\pi}\right)^3 \int d^3u \log \left(1 - e^{-\beta(u^2+\mu)}\right) \tag{15.7}$$

or

$$A = T\frac{\pi}{2} \left(\frac{\sqrt{2M}L}{\hbar\pi}\right)^3 \int u^2 du \log \left(1 - e^{-\beta(u^2+\mu)}\right) \tag{15.8}$$

Another form for A is obtained by defining $v = u^2$ (v is just the energy of a particle).

$$A = T\frac{\pi}{4} \left(\frac{\sqrt{2M}L}{\hbar\pi}\right)^3 \int \sqrt{v}dv \log \left(1 - e^{-\beta(v+\mu)}\right) \tag{15.9}$$

The average number of particles is given by $N = -\frac{\partial A}{\partial \mu}$. Dividing N by the volume we get the density of particles ρ.

$$\rho = \frac{\pi}{4} \left(\frac{\sqrt{2M}}{\hbar\pi}\right)^3 \int \sqrt{v}dv \frac{1}{e^{\beta(v+\mu)} - 1}. \tag{15.10}$$

We can see from (1.10) that μ must be positive or else the integral diverges. But as $\mu \rightarrow 0$ the density approaches a finite critical limit.

$$\rho_0 = \frac{\pi}{4} \left(\frac{\sqrt{2M}}{\hbar\pi}\right)^3 \int \sqrt{v}dv \frac{1}{e^{\beta v} - 1}. \tag{15.11}$$

or, letting $z = \beta v$

$$\rho_0 = \frac{\pi}{4} \left(\frac{\sqrt{2MT}}{\hbar \pi} \right)^3 \int \sqrt{z} dz \frac{1}{e^z - 1}. \tag{15.12}$$

The integral is approximately equal to 2.3. One finds

$$\rho_0 = \frac{0.165}{\hbar^3} (MT)^{3/2}. \tag{15.13}$$

We can also think of varying the temperature at fixed density. In this case a critical limit is reached when the temperature reaches

$$T_0 = \frac{3.3 \hbar^2}{M} \rho^{2/3}. \tag{15.14}$$

As that temperature is approached from the high temperature side, the chemical potential drops to zero. Alternately, at fixed temperature, when the density approaches ρ_0 the chemical potential becomes zero. Since μ must remain greater or equal to zero, it would appear that there is an obstruction to increasing the density or decreasing the temperature past the critical value. However, this is not correct. What does happen is that the approximation of going from a sum to an integral breaks down. In particular the integrand in (1.9) vanishes like $\sqrt{v}$ when $v \to 0$, but in the sum, the first term in (1.6) does not vanish. The first term represents particles with zero energy in the large volume limit. When the density grows above ρ_0 all the extra particles go into the lowest energy state. In other words, beyond the phase transition, the density is increased by increasing the number of zero energy particles. The number of such particles is

$$N_0 = V(\rho - \rho_0) \tag{15.15}$$

where V is the volume. The zero energy state is the only state that has a macroscopic number of particles (a finite fraction of the total), but only when the temperature is below the critical temperature. The macroscopic occupation of the ground state is called a Bose Einstein Condensate.

Below the phase transition in the Bose Einstein condensed phase, the chemical potential is zero and the free energy is

$$A = T \frac{\pi}{4} \left(\frac{\sqrt{2ML}}{\hbar \pi} \right)^3 \int \sqrt{v} dv \log \left(1 - e^{-\beta v} \right) \tag{15.16}$$

or

$$A = T^{\frac{5}{2}} \frac{\pi}{4} \left(\frac{\sqrt{2ML}}{\hbar\pi} \right)^3 \int \sqrt{z} dz \log\left(1 - e^{-z}\right) \tag{15.17}$$

.... Homework ....

Problem 15.1 For $T < T_0$ compute the energy, heat capacity, entropy, and pressure of the B.E. condensed gas.

....

The number of particles with energy greater than zero (those not in the zero-energy condensate) is obtained from (15.13):

$$N_{E>0} = \rho_0 V \sim V T^{3/2} \tag{15.18}$$

On the other hand for $T \geq T_0$ the total number of particles is essentially equal to the number with $E > 0$. So we expect that $N_{E>0} \rightarrow N_{total}$ as $T \rightarrow T_0$. We can write this in the form

$$N_{E>0} = N_{total} \frac{T^{3/2}}{T_0^{3/2}} \tag{15.19}$$

The remaining particles are those in the zero energy condensate:

$$N_{E=0} = N_{total} \left(1 - \frac{T^{3/2}}{T_0^{3/2}} \right) \tag{15.20}$$

A   Appendix A: Some basic mathematics

Transcendental functions

You should be familiar with the exponential and log functions (natural logs, not base-10 logs), trigonometric functions, and the hyperbolic functions

$$\sinh x \equiv \frac{e^x - e^{-x}}{2}$$

$$\cosh x \equiv \frac{e^x + e^{-x}}{2}$$

$$\tanh x \equiv \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

These are called the hyperbolic sine, cosine and tangent respectively, and are typically pronounced "cinch," "cosh," and "tanj" or "tan-h." Important formulas include

$$\frac{d}{dx} \sinh x = cosh x$$

$$\frac{d}{dx} \cosh x = \sinh x$$

$$\cosh^2 x - \sin^2 x = 1$$

Calculus

We assume you know the rules for differentiation (total and partial) and integration (definite and indefinite). The notation we use may be unfamiliar to you:

$$\int dx \; dy \; f(x, y)$$

means the same as

$$\int f(x, y) \; dx \; dy$$

Also $\partial_h A$ means $\partial A / \partial h$.

Probability

The idea of a probability *distribution* should be familiar to you. The area underneath a probability distribution between x_1 and x_2 is the probability of a result between those two limits. The best-known probability distribution is the normal or Gaussian distribution

$$P(z) = \frac{1}{\sqrt{2\pi}} e^{-z^2}$$

Necessarily,

$$\int_0^\infty P(z) dz = 1$$

Fourier transforms

Fourier analysis is a standard technique for converting periodic functions into trigonometric series. Given a function $f(t)$ defined on an interval from $-L$ to L, the Fourier series representation of $f(t)$ is

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^\infty \left(a_n \cos \frac{n\pi x}{L} + b_n \sin \frac{n\pi x}{L} \right)$$

where

$$a_n = \frac{1}{L} \int_{-L}^L f(x) \cos \frac{n\pi x}{L} \, dx, n = 0, 1, 2, \cdots$$

$$b_n = \frac{1}{L} \int_{-L}^L f(x) \sin \frac{n\pi x}{L} \, dx, n = 1, 2, 3, \cdots$$

Using the Euler identity $e^{i\theta} = \cos\theta + i\sin\theta$ we may write

$$f(x) = \frac{1}{2} \sum_{n=-\infty}^\infty c_n e^{i\omega_n x}$$

where $\omega_n = n * pi/L$ and

$$c_n = \frac{1}{L} \int_{-L}^L f(x) e^{-i*omega_n x} \, dx, n = 0, \pm 1, \pm 2, \cdots$$

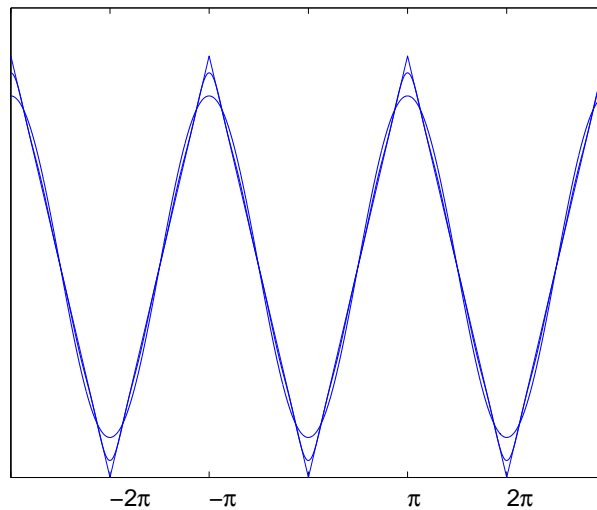A sawtooth function is shown in Figure 17 with approximations to $n = 1$ and $n = 7$.

Figure 17: A sawtooth wave approximated by one-term and four-term Fourier series.

Lagrange multipliers

The method of Lagrange multipliers allows us to find minimum or maximum values of a function subject to equality constraints. It is explained in many basic texts; wikipedia.org has a good short article on the subject.

We will illustrate the method with a function of two variables subject to a single constraint: minimize $f(x, y)$ subject to a constraint $g(x, y) = 0$ The minimum or maximum value of a function is found by setting its derivative(s) to zero, provided the function is suitably smooth.

The constraint function is a line in x, y space. The gradient at any point on that line is a vector perpendicular to the line $g(x, y) - c$. The gradient of the $f(x, y)$ is a vector perpendicular to its contour lines. A constrained maximum or minimum is found where the two vectors are perpendicular, i.e.,

$$\Delta f = \lambda \Delta g$$

where Δf is defined as the vector with components

$$\left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}\right)$$

λ is called a *Lagrange multiplier*. We solve the problem by minimizing (maximizing) an augmented function

$$\Lambda(x, y, \lambda) = f(x, y) + \lambda(g(x, y) - c)$$

Setting the three partial derivatives of this function to zero gives us three equations that can be solved for x_m, y_m (the coordinates where the function is minimized or maximized) and λ, the Lagrange multiplier:

$$\frac{\partial f}{\partial x} = 0$$

$$\frac{\partial f}{\partial y} = 0$$

$$\frac{\partial f}{\partial \lambda} = 0 = g(x, y) - c$$

This last equation is of course a restatement of the constraint equation.

As an example,[‡] maximize $f(x, y) = x + y$ subject to the constraint $x^2 + y^2 = 1$ The constraint is the unit circle and $f(x, y)$ is a tilted plane. Thus

$$\Lambda(x, y, \lambda) = f(x, y) + \lambda(g(x, y) - c) = x + y + \lambda(x^2 + y^2 - 1)$$

$$\frac{\partial \Lambda}{\partial x} = 1 + 2\lambda x = 0$$

$$\frac{\partial \Lambda}{\partial y} = 1 + 2\lambda y = 0$$

$$\frac{\partial \Lambda}{\partial \lambda} = x^2 + y^2 - 1 = 0$$

Solving these equations yields two solutions, $x_m = y_m = \sqrt{2}/2$, for which $f(x, y) = \sqrt{2}$ and $x_m = y_m = -\sqrt{2}/2$, for which $f(x, y) = -\sqrt{2}$

[‡]Source: wikipedia.org

B   Appendix B: Phase space

We are all familiar of two-dimensional plots with some physical variable shown on each axis, such as PV diagrams (pressure versus volumes). *Phase space* is a generalization of this idea to multiple dimensions. Concepts like line, area, and volume are likewise generalizations of geometric concepts. Thus an "area" on a PV diagram has dimensions of pressure times volume (force per unit area times volume = force times length = energy).

You should have no difficulty as long as you remember that areas and volumes in phase space are not geometric concepts.

C   Appendix C: Ludwig Boltzmann

Ludwig Boltzmann (1844-1906) was Professor of Physics at the University of Vienna and the last of the great classical physicists. He viewed the Second Law as a manifestation of probability, but struggled to establish a clear relationship. Then it occurred to him that probabilities are multiplicative while entropy and other extensive quantities are additive. What function takes multiplicative properties into additive properties? One day it occurred to him the logarithm function just does that. For a brief time, Boltzmann found himself in that elevated state, one that all scientists dream of and a few occasionally achieve: having discovered something important that no one else yet knew. His famous formula is inscribed on his tombstone in Vienna (Figure 18).

Figure 18: Ludwig Boltzmann's tomb, inscribed with $S = \log P$

Ludwig Boltzmann was a colorful character to say the least.*. He was a large man, accustomed to consuming copious quantities of food and drink. He was a fine pianist

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*von Baeyer, "Maxwell's Demon," Random House, 1998, Chapter 13

and once performed Schubert sonatas for William Randolph Hearst. In 1905, though in ill health, he undertook a grueling journey from Vienna to Berkeley to deliver a summer series of lectures. He found to his dismay that the City of Berkeley was dry. But he soon learned to smuggle cases of wine across the line from Oakland.

Sadly, Boltzmann suffered from depression and perhaps bipolar disorder. Not long after his return to Vienna in 1906, he took his own life.

D   Appendix D: for Engineers

Engineers and physicists labor in somewhat different worlds and each group has certain conventions that suit their purposes. Readers who have been trained in engineering thermodynamics may need to be careful about adjusting to the conventions in this book, especially dimensions and units.

Some common engineering units in thermodynamics are as follows:

	SI units	English units
Temperature	C, K	F, R
Energy	joule (J)	ft-lb
Power	watt (w)	hp, ft-lb/sec
Entropy	J/K	ft-lb/R
Boltzmann's constant k ($S = k \log P$)	1.38×10^{-23} J/K	1.04×10^{-23} ft-lb/F
Stefan-Boltzmann constant σ ($\dot{q} = \sigma T^4$)	5.67×10^{-8} W/m^{2}K^4	0.1714×10^8 BTU/hr ft^2 R^4

In this text, T has units of energy and can be thought of as equal to kt where t is the "textbook temperature" in degrees K (SI units), and k is Boltzmann's constant in J/K. Also, we measure entropy in bits, a dimensionless quantity, as contrasted with the engineering definition that involves a factor of k, again in J/K.

There should be no difficulty with units as long as you remember to include the proper constants when performing numerical calculations.